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STUDIES ON THE DIELECTRIC PROPERTIES OF ORGANIC SOLVENT II. A NEW FORMULA ON THE REFRACTIVE INDEX OF ORGANIC BINARY SOLVENT SYSTEM

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1) INTRODUCTION

As shown in previous papers, we found theoretically that there is a simple additivity law in which the reciprocal number of dielectric constant of a mixed solvent is represented by the sum of the reciprocal numbers of dielectric constants of the pure solvents at the rate of weight fraction.[1)2)] This additivity law is effectively applicable in the case when the molecules of components have no mutual interaction. The first work in proving the above law was undertaken with the system of various kinds of organic substances that have very small dipole moments.[1)] The results of the experiments showed good agreements with the theoretical values and were throughly compatible in proving the above mentioned law.

Similar relationship on the density of the mixed solvent was also introduced and the reliability of the formula was recognized[3)] with good conformity to the experimental values. These additivity laws on the dielectric constant and the density of a mixed solvent are respectively shown in the following formulas :

$$\frac{1}{\varepsilon_{i+j}}=\frac{w_i d_j}{\varepsilon_i(w_i d_j+w_j d_i)}+\frac{w_j d_i}{\varepsilon_j(w_i d_j+w_j d_i)} \cdots\cdots 1)$$

$$\frac{1}{d_{i+j}}=\frac{w_i}{d_i}+\frac{w_j}{d_j} \cdots\cdots 2)$$

In these above formulas, w_i and w_j are the weight fractions, d_i and d_j are the densities and the suffix i and j respectively denote the species of the corresponding pure solvents i and j. These additivity laws can be practically applicable only in the case when the mutual interactions of the component molecules are very small. However, in general cases, when the molecules have large amounts of dipole-moments, the deviasions which were calculated from the above formulas reach to some extent and can not practically use them for any arbitrary solvent mixtures.

Thus, the formula 1) on the dielectric constant of the mixed solvent was transformed into the following form with the compensation of the effect of such molecular interactions.

$$\frac{1}{\varepsilon_{i+j}}=\frac{w_i d_j}{\varepsilon_i(w_i d_j+w_j d_i)}+\frac{w_j d_i}{\varepsilon_j(w_i d_j+w_j d_i)}-\frac{\beta\cdot w_i w_j}{(w_i M_j+w_j M_i)(w_i d_j+w_j d_i)} \cdots\cdots 3)$$

The results of the experiments which were undertaken to examine the conformity of this formula were very satisfactory. In the formula 3), M_i and M_j are the molecular weights, β is a constant which is characteristic to the system and is determined empirically by using the value of dielectric constant of the mixed solvent in equal weight fractions.

In the present paper, the writer intends to expand the formula 1) into the refractive index of any kind of mixed solvents by introducing Maxwell theory denoting that the dielectric constant of a substance can be reffered to the refractive index of the similar medium. The conformity of the resulted formula to the experimental values was examined by using benzene dioxane binary solvent mixtures.

2) THEORETICAL

As we well known, Maxwell theory concerning the propagation of an electromagnetic wave in a dipole medium shows us that the refractive index is related to the dielectric constant in the form of $n^2=\varepsilon$, and this simple relation is indifferent to the temperature of the medium. In the limited case when the frequency of the electromagnetic wave used in the measurement is almost equall to that of light, the refractive index, which was expressed in the above relation, may be applicable to the formula 1) instead of the dielectric constant. As already mentioned before, we have assumed the ideal case in introducing the formula 1) that the molecules of the considering mixture have no mutual interaction as likely to the case of ideal gases.

Accordingly, Maxwell relation can be introduced into the formula 1) with no contradictions. But in the liquid state under consideration, some differences may be presumably expected between the observed values and the calculated values. These differences will, perphaps, be attributed to the effect of an induced atomic polarizations which were introduced as the result of the weak interactions in the liquid state. Undoubtedly, such errors give some usefull informations for us in the studies of the mechanisms of such interactions in the binary solvent mixtures.

By putting Maxwell relation into the formula 1), we have :

$$\frac{1}{n^2{}_{i+j}}=\frac{w_i d_j}{n_i{}^2(w_i d_j+w_j d_i)}+\frac{w_j d_i}{n_j{}^2(w_i d_j+w_j d_i)}\cdots\cdots 4)$$

The formula 4) involves a new conception that the refractive index of any binary solvent mixture can be calculated theoretically from three elements ; the density, the refractive index and the weight fraction of the pure components of the binary solvent mixture.

3) EXPERIMENTAL

The measurements of the dielectric constants were undertaken with sinsoidal wave of 1 Mc/s, 10c/s, 5c/s and 1c/s respectively at 25° ±0.01, by using *TR*-10C and *TRS*-4 Type of dielectric analyser of Ando Electric Company. The cell used was *LE*-1 Type cell for liquid use with guard electrode. The *mean* values of the dielectric constants of pure benzene and dioxane measured in high frequency band were slightly low in compared with the values measured in ultra low frequency band i. e. ; 2.2353 and 2.1925 for 1

Mc/s., 2.2775 and 2.2234 for 1 c/s at 25°C±0.05 respectively.

The measurements of the refractive indices were undertaken by the use of Abbe's New Type refractometer at 30°C±0.1 or 35°C±0.1. The temperature of the sample was exactly controlled by circulating the water of fixt temperature from the thermostat. The temperature of the thermostat was regulated by Ostward's mercury regulator and electron tube relay at 25°C±0.01, or 35°C±0.02. The solvents used, benzene and dioxane, were special grade of commercial use. These solvents were exactly isolated from moisture during the experiments.

4) DISCUSSION

The refractive indices measured in the full ranges of the composition were illustrated in Tables 1) and 2) with the comparison of the calculated values according to the formula 4). The dielectric constants of the above composition were also given in Tables 3) 4) and 5). As clearly shown in these tables, the conformity of the calculated values of the refractive index and the dielectric constant to the observed values was very satisfactory. In this experiment, it must be noted that the *mean* error of the refractive indices calculated from the formula 4) was estimated to be below 0.01 percent.

This high degree of agreement in the refractive indices shows us that the hypothesis used in the derivation of the formulas 1) and 4) were throughly affirmative. The hypothesis which were used in the derivation of the formula 4) is essentially identical to that of the formula 1). And, owing to the use of refractive index, the time of relaxation of the considering molecules is far beyond of the time of alternation of the applied field. Accordingly, the compensation term of the right hand of the formula 3) is practically omitted.

The slight deviasions which were observed in the refrsctive indices may be attributed to the very weak deformation of the atomic orbitals due to the mutual interactions between benzene and dioxane molecules in the liquid state.

Figures 1) and 2) respectively show the change of the dielectric constant and of the refractive index with related to the composition. As clearly shown in the figure 1), the

TABLE 1). Refractive Index of Benzene-Dioxane Mixture at 30°C.
i = Benzene, j = Dioxane.

w_i	w_j	n_D (calc.)	n_D (obs.)	Δ	Δ %
1.00000	0.00000	1.49483	1.49483	0.00000	0.00000
0.79649	0.20351	1.48001	1.48000	0.00001	0.00067
0.59954	0.40046	1.46502	1.46473	0.00029	0.01979
0.55215	0.44785	1.46156	1.46250	0.00094	0.06416
0.49537	0.50463	1.45716	1.45590	0.00126	0.08646
0.44404	0.55596	1.45315	1.45380	0.00065	0.04473
0.40096	0.59904	1.44977	1.44943	0.00034	0.02193
0.34408	0.65592	1.44525	1.44567	0.00042	0.02911
0.29777	0.70223	1.44099	1.44099	0.00000	0.00000
0.19739	0.80261	1.43343	1.43190	0.01530	0.10607
0.00000	1.00000	1.41702	1.41702	0.00000	0.00000

TABLE 2). Refractive Index of Benzene-Dioxane Mixture at 35°C.

wi	*wj*	*nD* (calc.)	*nD* (obs.)	Δ	Δ %
1.00000	0.00000	1.49145	1.49135	0.00010	0.00670
0.89944	0.10056	1.48422	1.48413	0.00009	0.00606
0.84054	0.15946	1.48236	1.47665	0.00571	0.38519
0.70052	0.29948	1.46985	1.46943	0.00042	0.02857
0.63107	0.36893	1.46469	1.46135	0.00334	0.22803
0.52749	0.47251	1.45688	1.45423	0.00423	0.29034
0.47417	0.52583	1.45281	1.45048	0.00233	0.16037
0.40811	0.59189	1.44772	1.44775	0.00017	0.01174
0.30172	0.69828	1.43942	1.43942	0.00000	0.00000
0.20514	0.79486	1.43173	1.43185	0.00008	0.00558
0.14877	0.85123	1.42708	1.42713	0.00005	0.00350
0.09225	0.90775	1.42260	1.42275	0.00015	0.01054
0.00000	1.00000	1.41500	1.41500	0.00000	0.00000

TABLE 3). Dielectric Constant of Benzene-Dioxane Mixture, 1 c/s, at 25°C.
i = Beuzene, j = Dioxane.

wi	*wj*	ε_{i+j} (obs.)	ε_{i+j} (calc.)	Δ	Δ %
1.00000	0.00000	2.2796	2.2796	0.0000	0.0000
0.86231	0.13769	2.2739	2.2754	0.0015	0.0659
0.77533	0.22467	2.2719	2.2726	0.0007	0.0303
0.65102	0.34898	2.2689	2.2684	0.0005	0.0220
0.55983	0.44107	2.2654	2.2650	0.0004	0.0176
0.45864	0.54136	2.2614	2.2610	0.0004	0.0176
0.34090	0.65900	2.2581	2.2561	0.0020	0.0885
0.17517	0.82483	2.2537	2.2485	0.0052	0.2307
0.09824	0.90176	2.2490	2.2447	0.0043	0.1947
0.00000	1.00000	2.2396	2.2396	0.0000	0.0000

TABLE 4). Dielectric Constant of Benzene-Dioxane Mixture, 5 c/s, at 25°C.

wi	*wj*	ε_{i+j} (obs.)	ε_{i+j} (calc.)	Δ	Δ %
1.00000	0.00000	2.2796	2.2796	0.0000	0.0000
0.86231	0.13769	2.2738	2.2752	0.0014	0.0633
0.77533	0.22467	2.2716	2.2723	0.0007	0.0312
0.65102	0.34898	2.2682	2.2678	0.0003	0.0154
0.55983	0.44017	2.2646	2.2643	0.0002	0.0106
0.45864	0.54136	2.2607	2.2603	0.0004	0.0141
0.34091	0.65909	2.2574	2.2554	0.0020	0.0881
0.17517	0.82483	2.2531	2.2477	0.0054	0.2361
0.09824	0.90176	2.2491	2.2440	0.0051	0.2245
0.00000	1.00000	2.2390	2.2390	0.0000	0.0000

TABLE 5). Dielectric Constant of Benzene-Dioxane Mixture, 10 c/s, at 25°C.

w_i	w_j	$\varepsilon\ i+j$ (obs.)	$\varepsilon\ i+j$ (calc.)	Δ	Δ %
1.00000	0.00000	2.2798	2.2798	0.0000	0.0000
0.86231	0.13769	2.2740	2.2755	0.0015	0.0686
0.77533	0.22467	2.2717	2.2726	0.0009	0.0414
0.65102	0.34898	2.2680	2.2682	0.0002	0.0088
0.55983	0.44017	2.2646	2.2647	0.0001	0.0044
0.45864	0.54136	2.2609	2.2606	0.0003	0.0132
0.34091	0.65909	2.2576	2.2554	0.0022	0.0943
0.17517	0.82483	2.2526	2.2475	0.0051	0.2224
0.09824	0.90176	2.2480	2.2436	0.0044	0.1940
0.00000	1.00000	2.2383	2.2383	0.0000	0.0000

Fig. 1. The Dielectric Constant of Benzene-Dioxane Mixture.

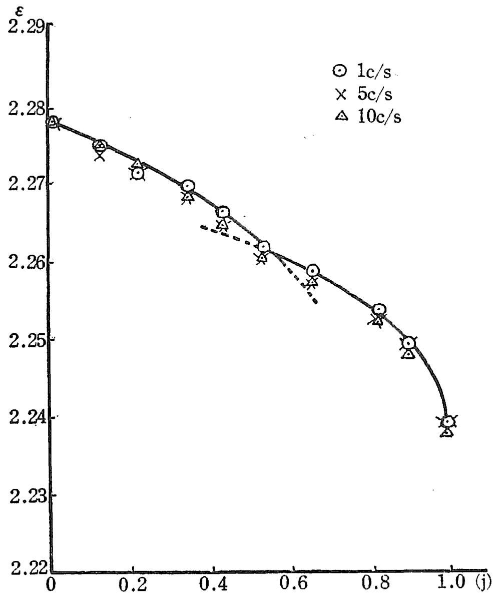
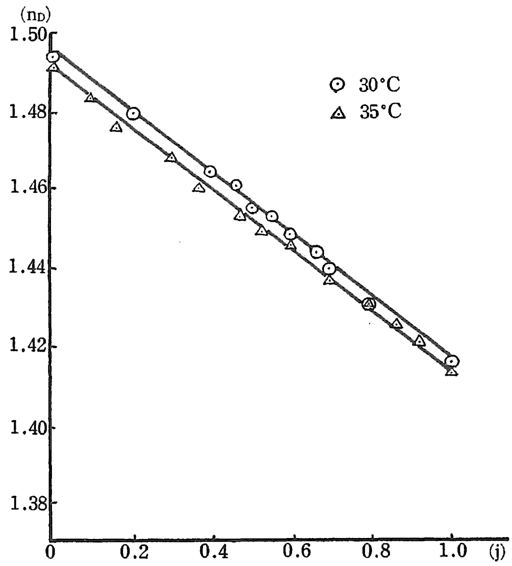


Fig. 2. The Refractive Index of Benzene-Dioxane Mixture.



curve of the dielectric constant of the mixed solvent has an inflextion point in the region of equi-molar fraction ($j=0.57$). This fact gives us some informations that the molecules of benzene and dioxane seems to conbine at the proportion of 1 : 1 in molecular ratio. On this problem, we had further investigations from the viwpoint of viscosity analysis, and the datas obtained through this investigation were also good agreement with the results of the dielectric analysis.

The detailes on this problem will be published in the following papers.

LITERATURES

1) Senseki Takano ; Studies on the dielectric properties of organic solvents (1), Part 2, A New Equation on the Dielectric Constant of Binary Organic Solvent Mixtures. *Mem. Fac. of Education, Shimane Univ.*, vol. **1**. 31 (1967).

2) Senseki Takano ; A Critical Discussion on the Solubility Equation of Slightly Soluble Salts, ; A New Concept on the Effective Dielectric Constant of Mixed Solvent. *Mem. Niihama Tech. Coll.* vol. **2**. 29 (1966).

3) Senseki Takano ; Appendix 2) of Lit. 1), and, Akira Yamamoto and Senseki Takano ; The Molecular Interaction Observed in the Specific Volume of Organic Binary Mixtures. *Bull. Shimane Univ.* No. **16**, 98 (1966).