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STUDIES ON THE DIELECTRIC PROPERTIES OF ORGANIC SOLVENTS IV.

A COMPARATIVE DISCUSSION ON THE IDENTITY OF VARIOUS VISCOSITY EQUATIONS WITH RESPECT TO TAKANO VISCOSITY EQUATION

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I. INTRODUCTION

The viscosity of a mixed solvent of organic substances has already been discussed by many researchers of this field since Poiseulle took up at first his work on the viscosity of alcohol-water mixed solvent, and the analysis of many viscosity curves related to the composition has been studied chiefly from the theoretical approach and under the object of experimental certification[1)]. However, even the successfull hitness of applying the kinetic theory of gas to the viscosity of gas mixture, the application of it for elucidating the mechanisum of viscosity of liquid mixture was not so effective at all owing to the strong molecular interaction in the liquid state.

Different from the gas molecules, the molecules of liquid are in restricted state under the molecular field, and even the most simple case when the stoichiometric evaluation can be presumably expected or even in no chemical reaction between the liquid molecules included, the theoretical equation by which the viscosity of the mixed solvent can be completely descrived has not been introduced.

Naturally, the viscosity can be defined as a mechanical friction of discontinuous particles in a liquid movement, so the shape of molecule and the internal force acted upon the moving molecules were considered to be basic factors and many works of investigations have been performed chiefly from these points of view, however, as it has been pointed out in our previous papers[2)], it is very doubtfull to think simply that the direct confliction of the molecules gives such mechanical restriction in the velocity gradient of the liquid flow.

We have already introduced the idea of interacting space of a molecule and also recognized that the restrictive force in a liquid flow is consequently attributed to the sum of the forces which appeared in the above mentioned space. Thus the viscosity of a liquid is effectively descrived with the probability of the molecules penetrated into the interacting space. Based upon the above mentioned idea, a new equation of viscosity was introduced theoretically and was examined with the use of benzene-dioxane mixed solvent system.

In the first stage of viscosity investigation, the association of the liquid molecules was taken up as an important factor in a mixed solvent system and this trend of work

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opened up a new ways of analysing the process of polymerization in high polymer chemistry. One of the researchers in Japan who first took up this problem into pure science of viscosity investigation was Dr. Ishikawa[3]. He successfully introduced the effect of polymerization into his viscosity equation as a constant which was defined as a ratio of the product of association constant and the force constant of the given media.

In 1923, Myer and Milius[4] expanded Batshinsky Equation[5] for the bicomponent system in which the law of additivity for the specific volume is applicable. Myer-Milius Equation was derived from such a point of view that the fluidity of a liquid corresponds to the free space of the molecule. The Ishikawa Equation was originally started from the different idea from the above one that the additivity rule holds only to the viscosity itself in spite of the fluidity. Accordingly, in Ishikawa Equation, although the association of liquid molecules was taken into account, likely to the Myer-Milius Equation, the mutual interaction between the liquid melecules was originally disregarded.

In this paper, the identity of these viscosity equations to the experimental results was discussed in comparing with the Takano Equation[6] and was elucidated the nature of dioxane-cyclohexane mixed solvent system through the viscosity investigations.

II. THEORETICAL

The brief explanations of the equations are as follows ;

1) Myer-Milius Equation.

This equation of viscosity was derived by Myer and Milius in 1920. And the theoretical base of this equation is taken from the Batshinsky Equation ;

$$\eta = C/(v-w) \quad \cdots\cdots \quad 1)$$

where η denotes the viscosity, C and w are constants, v the specific volume. As clearly seen above, this equation shows that the viscosity of a liqiud is invesely proportional to the specific volume or the free space of a molecule according to Macleod[7] (1923).

By expanding this equation to the components i, j and $i+j$, the mixture, we have ;

$$\left.\begin{array}{l} v_i = w_i + C_i\varphi_i \\ v_j = w_j + C_j\varphi_j \\ v_{i+j} = w_{i+j} + C_{i+j}\varphi_{i+j} \end{array}\right| \quad \cdots\cdots \quad 2)$$

By assuming the additivity rule for the specific volumes v_i, v_j and v_{i+j}, the mixed solvent, and by denoting the weight fraction of the component j with z, we have ;

$$v_{i+j} = v_i(1-z) + v_j z \quad \cdots\cdots \quad 3)$$

From Eq. 2) and Eq. 3) we have ;

$$\left.\begin{aligned}\varphi_{i+j}&=\varphi_i\frac{C_i}{C_{i+j}}(1-z)+\varphi_j\frac{C_j}{C_{i+j}}z\\&=\alpha\varphi_i(1-z)+\beta\varphi_j z\end{aligned}\right| \quad\cdots\cdots\cdots\cdots\cdots\cdots \quad 4)$$

where C_i and C_j are constants, C_{i+j} is the similar constant of the mixture $i+j$, the values α and β are respectively defined as ;

$$\alpha=C_i/C_{i+j}\,,\ \beta=C_j/C_{i+j}$$

Accordingly, this equation can be applied only for the calculation of the viscosity of the mixture of two solvents having fluidity φ_i and φ_j if the constants α and β are determined. And it is worthly mentioned that this viscosity equation holds true only in the case when the molecules of the components i and j have no mutual interaction and the additivity rule on the specific volumes is completely admitted.

2) Ishikawa Equation and Ishikawa-Baba Equation.

The former viscosity equation was first introduced by Ishikawa[3)] in 1929. The important and characteristic points of this equation are started from the idea that when the molecules of liquid are associated and make a cluster, the viscosity of the liquid can be expressed by the number of the cluster. On the above mentioned cluster formation, he put two assumptions that 1) the associated molecules in the liquid act,as an independent component for single molecules and 2) the association of the liqnid molecules is resulted from the force of molecular field.

From these assumptions, he considered that the viscosity of a mixed solvent must be descrived at least by using the following two variables ; 1) the effective numbers of associated molecules and 2) the mean strength of the molecular field. He introduced these ideas into Macleod Equation as a new variable Z'_m in spite of Z' as follows ;

$$z'_m=\frac{k_ja_jn_j}{k_ia_in_i+k_ja_jn_j}=\frac{k_ja_jz_m}{k_ia_i(1-z_m)+k_ja_jz_m} \quad\cdots\cdots\cdots\cdots\cdots\cdots \quad 5)$$

where n_i and n_j are the number of molecules of pure solvents i and j, k_i and k_j are the constants concerning the molecilar field i and j, a_i and a_j are the degree of association, Z_m the molar fraction of j and Z'_m the effective molar fraction according to Eq. 5).

By applying Z'_m into Macleod Equation we have ;

$$\eta_{i+j}=\eta_i(1-z'_m)+\eta_jz'_m \quad\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \quad 6)$$

From Eq. 5) and Eq. 6) we have ;

$$\eta_{i+j}=\frac{\eta_i}{1+K\dfrac{z_m}{1-z_m}}+\frac{\eta_j}{1+\dfrac{1}{K}\dfrac{1-z_m}{z_m}} \quad\cdots\cdots\cdots\cdots\cdots\cdots \quad 7)$$

where

$$k_j a_j / k_i a_i = K \quad \cdots\cdots 8)$$

Later in 1930, Ishikawa and Baba[8)] modified this equation by transforming the constant a_i or a_j into a_i' or a_j''. This transformation is based on the following idea that if the molecule i is present in the large amount of liquid j, then the association constant a_i is not the same as that of pure liquid i, and it will vary into a_i' owing to the effect of different kinds of molecular field of pure liquid j. As same as the above case, the value a_j varies into a_j''. This idea means that the constant K in Ishikawa Equation is not constant and varies with the molar fraction Z of the j component. Putting these relations into constant K in Eq. 6), we have ;

$$K' = k_j a_j' / k_i a_i, \quad K'' = k_i a_i / k_j a_j'' \quad \cdots\cdots 9)$$

By putting these constants K', K'' into Ishikawa Equation we have ;

$$\eta_{i+j} = \frac{\eta_i}{1 + K' \dfrac{z_m}{1 - z_m}} + \frac{\eta_j}{1 + K'' \dfrac{1 - z_m}{z_m}} \quad \cdots\cdots 10)$$

These equations 7) and 10) are respectively called the Ishikawa Equation and Ishikawa-Baba Equation and the former can be applied to the ideal mixture and the latter to the non-ideal mixture respectively.

3) Takano Equation

This viscosity equation differs from the above mentioned ones in the theoretical derivation. In this equation, the viscosity of a mixed solvent is assumed to be expressed as the summation of the restrictive forces which will be attributed to the mutual interactions of the pairs of molecules $i-i$, $j-j$ and $i-j$ in the liquid flow. And these restrictive forces also assumed to be expressed as the number of pairs, thus we have ;

$$F_{i+j} = P_{ii} F_{ii} + P_{jj} F_{jj} + P_{ij} F_{ij} \quad \cdots\cdots 11)$$

where P_{ii}, P_{jj} and P_{ij} are the probability functions and these are denoted with n_i^2, n_j^2 and $n_i \times n_j$ respectively, where n_i and n_j are the number of molecules in a unit space. Accordingly, by the definition of viscosity, we have ;

$$\eta_{i+j} \frac{\partial U}{\partial x} = k_{ii} n_i^2 \eta_{ii} \frac{\partial U}{\partial x} + k_{jj} n_j^2 \eta_{jj} \frac{\partial U}{\partial x} + k_{ij} n_i n_j \eta_{ij} \frac{\partial U}{\partial x} \quad \cdots\cdots 12)$$

Consequently, the above equation can be transformed into by using the characteristic constants of the pure solvents i and j as follows ; [2)].

$$\eta_{i+j}=\frac{d_i^2\,d_j^2}{(w_i d_j+w_j d_i)^2}\,(\lambda w_i^2\eta_{ii}+\mu w_j^2\eta_{jj}+\nu w_i w_j\eta_{ij})\cdots\cdots\cdots\cdots\cdots\cdots\quad 13)$$

where

$$\left.\begin{aligned}\lambda&=1/d_i^2\\ \mu&=1/d_j^2\\ \nu&=\frac{\eta_{ij}(M_i d_j+M_j d_i)^2-M_i^2 d_j^2\eta_{ii}-M_j^2 d_i^2\eta_{jj}}{d_i^2 d_j^2 M_i M_j\eta_{ij}}\end{aligned}\right|\cdots\cdots\cdots\cdots\cdots\cdots\quad 14)$$

The symboles used in this equation are ; d_i or d_j the density, w_i or w_j the weight fraction, M the molecular weight, η_i or η_j respectively the viscosity coefficient of pure solvent i or j, and η_{ij} the hypothetical viscosity due to the mutual interaction of the molecules i and j. Empirically the value η_{ij} can be replaced with that of measured in the equimolar mixtures.

III. EXPERIMENTAL and RESULTS

The materials used were dioxane and cyclohexane of spectro-analysis grade without home purification. The refractive indices of these materials exhibited 1.4201 for dioxane and 1.4236 for cyclohexane at 25°C. The dielectric constants measured at 10 c/s were 2.239 for dioxane and 2.036 for cyclohexane at 25°C, and the densities measnred at 25°C were 1.0297 for dioxane and 0.7769 for cyclohexane respectively. From these pure solvents, a series of the mixtures having various weight fractions was prepared. These systems of mixed solvents were used both for the purpose of examining the mutual interaction by the viscosity measurements and also the dipole moment measurements. On the discussion of the molecular interaction, the detailes of the investigation will be published in this Memoirs in near future and will not be discussed here.

The viscosity measurements were undertaken by the use of Ostwald's viscosimeter. In oder to avoiding the error due to evaporation of sample, the measurements were opened ten minutes after from the end of setting the viscosimeter in thermostat. The temperature of the thermostat was exactly kept at 25°C and 20°C respectively with the variation of ± 0.01°C. The absorption of moisture to dioxane was strictly avoided. The pipettes and bottles for preparing the mixture were also dried out with dried air stream before preparation. The above treatment is very significant especially in the case of dielectric observation. The refractive index was measured by the use of Abbe's New Type refractometer with the accuracy of ± 0.01°C of temperature controle. The dielectric constant was measured at two different frequencies of 10 c/s and 1 Mc/s with the use of Ando's TR-4 Type and TR-10 Type Dielectric Loss Analyser. The measurements of density or specific volume were undertaken by the use of an Ostwald's Type picknometer. The results of measurements are shown in Tables 1, 2, 3 and 9.

1) The Density of Dioxane-Cyclohexane Mixture.

The certification of the additivity rule for the specific volume or density of this system is very important through these investigations. As clearly shown in Myer-Milius Equation and also in Takano Equation, these are both derived from the assumption that the specific volume of the mixed solvent examined must be satisfied the additivity law. Table 1 shoews the experimental results. The theoretical value of the density $(d_{i+j})_c$ and the specific volume $(v_{i+j})_c$ were respectively calculated according to Eq. 3). As clearly shown in Table 1, the additivity law was clearly recognized.

Table 1. The Density of Dioxane-Cyclohexane System.
i ; Dioxane, j=Cyclohexane**
$d_i=1.02958$, $d_i=0.77463$, at 25°C.

w_i	w_j	$A=w_i/d_i$	$B=w_j/d_j$	$A+B$	$(d_{i+j})_c$*	$(d_{i+j})_o$	△
0.00000	1.00000	0.00000	1.29093	1.29093	0.77463	0.77463	0.00000
0.08719	0.91281	0.08468	1.17838	1.26306	0.79172	0.78843	0.00329
0.24861	0.75139	0.24146	0.96999	1.21145	0.82545	0.81863	0.00682
0.43628	0.56372	0.42374	0.72772	1.15146	0.86846	0.86011	0.00835
0.47250	0.52750	0.45926	0.68075	1.14001	0.87718	0.86804	0.00914
0.53779	0.46221	0.52233	0.59668	1.11901	0.89364	0.88450	0.00914
0.57260	0.42740	0.55650	0.55157	1.10813	0.90242	0.89380	0.00862
0.60556	0.39444	0.58816	0.50919	1.09735	0.91128	0.90215	0.00913
0.66500	0.33500	0.64637	0.43232	1.07869	0.92705	0.91840	0.00865
0.69726	0.30274	0.67722	0.39081	1.06803	0.93630	0.92842	0.00788
0.75760	0.24240	0.73637	0.31282	1.04919	0.95311	0.94607	0.00704
0.84196	0.15804	0.81777	0.20401	1.02178	0.97868	0.97300	0.00568
0.95029	0.04971	0.92298	0.06417	0.98715	1.01301	1.01063	0.00238
1.00000	0.00000	0.97126	0.00000	0.97126	1.02958	1.02958	0.00000

* The calculations of density were performed according to Eq. 3), △ shows the difference betw. the calculated value $(d_{i+j})_c$ and the observed value $(d_{i+j})_o$.

** The samples used were different from those of Table 2 or 3.

2) The Viscosity of Dioxane-Cyclohexane Mixture.

Tables 2 and 3 respectively show the observed viscosity of dioxane-cyclohexane mixture at 20°C and 25°C. The calculations of the relative viscosity from the observed values of the elusion time were performed by using the calculated datas of the density d_{i+j} in any weight fraction Z according to Eq. 3). As shown in Figure 1, the viscosity-composition relation showed a typical catenary curve. In the present system of dioxane-cyclohexane mixture, a knick point at the near of equimolar composition which was often observed in the case of dioxane-benzene mixture was not recognized.

3) The Certification of Identity.

Tables 4, 5, 6 and 7 respectively show the identity of the observed viscosities and the calculated ones according to Myer-Milius, Ishikawa, Ishikawa-Baba and Takano Equations in dioxane-cyclohexane mixed solvent system at 20°C or 25°C. These equations used for the calculation of viscosity were respectively estimated by introducing the elements of calculation at the corresponding temperatures as follows ;

Table 2. The Viscosity of Dioxane-Cyclohexane System.
i ; Dioxane, j ; Cyclohexane
$d_w = 0.99704$, $t_w = 272.920$, $d_w \times t_w = 272.1132$, 25°C

Exp. No.	w_i	w_j	z_{mj}	$(d_{i+j})_c$*	t	$(d_{i+j}) \times t$	$(\eta_{i+j}) \times_o$
0	1.00000	1.00000	1.00000	0.77699	351.570	273.1663	1.00019
8	0.08697	0.91303	0.91667	0.79399	331.000	262.8100	0.96581
12	0.23429	0.76571	0.77382	0.82439	311.226	256.5716	0.94288
19	0.36305	0.63095	0.64949	0.85300	303.490	258.8769	0.95135
33	0.42948	0.57052	0.58174	0.86855	302.007	262.3081	0.96396
35	0.48728	0.51272	0.52419	0.88254	301.838	266.3841	0.97894
41	0.54568	0.45432	0.46573	0.89715	302.466	271.3573	0.99722
42	0.59764	0.40230	0.41342	0.91055	303.934	276.7471	1.01702
44	0.65262	0.34738	0.35184	0.92518	306.500	283.5676	1.04209
45	0.70351	0.29649	0.30612	0.93915	309.848	290.9937	1.06938
46	0.75632	0.24368	0.25220	0.95409	313.987	299.5718	1.10090
47	0.85435	0.14565	0.15140	0.98314	325.126	319.6443	1.17467
48	0.94934	0.05066	0.05289	1.01302	340.940	345.3790	1.26924
100	1.00000	0.00000	0.00000	1.02971	351.836	362.2890	1.33139

* These values of density were calculated according to Eq. 3.

Table 3. The Viscosity of Dioxane-Cyclohexane System.
i ; Dioxane, j ; Cyclohexane
$d_w = 0.99820$, $t_w = 306.730$, $d_w \times t_w = 306.788$, 20°C.

Exp. No.	w_i	w_j	z_{mj}	$(d_{i+j})_c$*	t	$(d_{i+j})_c \times t$	$(\eta_{i+j})_o$
0	0.00000	1.00000	1.00000	0.77957	381.018	297.0302	0.97012
8	0.08618	0.91382	0.91741	0.79651	358.250	285.3497	0.93197
12	0.16143	0.83857	0.84468	0.81192	345.245	280.3113	0.91551
19	0.23329	0.76671	0.77485	0.82720	336.002	277.9408	0.90777
7	0.30266	0.69734	0.70696	0.84251	330.365	278.3358	0.90906
35	0.36956	0.63044	0.64109	0.85782	327.143	280.6298	0.91655
41	0.45625	0.54375	0.55509	0.87851	325.508	285.9620	0.93397
42	0.53749	0.46251	0.47394	0.89881	326.188	293.1810	0.95754
44	0.61384	0.38610	0.39707	0.91877	328.570	301.8802	0.98596
45	0.68933	0.31067	0.32057	0.93940	332.876	312.7037	1.02131
46	0.76939	0.23061	0.23883	0.96232	340.192	327.3735	1.06922
47	0.84331	0.15669	0.16283	0.98449	349.504	344.0831	1.12379
48	0.91126	0.08874	0.09251	1.00577	361.250	363.3416	1.18669
1	1.00000	0.00000	0.00000	1.03504	381.532	394.9008	1.28977

* These values of density were calculated according to Eq. 3.

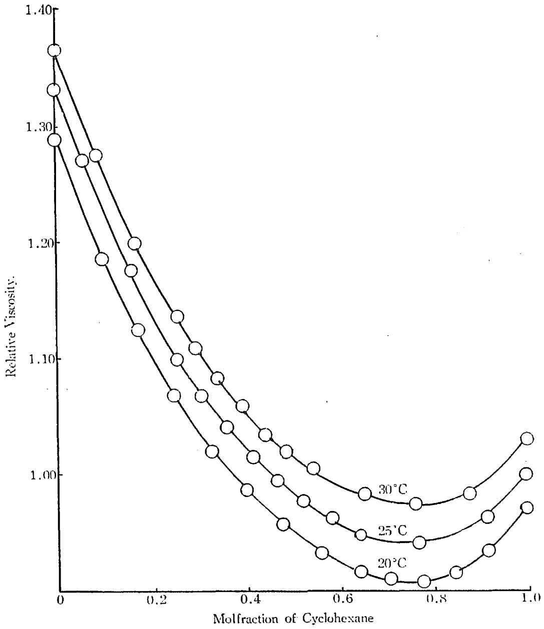

Figure 1. The Viscosity of Dioxane (i)-Cyclohexane (j) Mixture.

Myer-Milius Equation (20°C).

$$\varphi^{20}_{i+j}=1.1075\varphi_i w_i+1.1117\varphi_j w_j \quad \cdots\cdots \quad 15)$$

Ishikawa-Baba Equation (20°C).

$$\eta^{20}_{i+j}=\frac{\eta_i}{1+1.4167\frac{z_m}{1-z_m}}+\frac{\eta_j}{1+1.4092\frac{1-z_m}{z_m}} \quad \cdots\cdots \quad 16)$$

Takano Equation (20°C and 25°C).

$$\eta^{20}_{i+j}=\frac{d_i^2 d_j^2}{(w_i d_j+w_j d_i)^2}(1.2039w_i^2+1.5963w_j^2+1.9886w_i w_j) \cdots\cdots 17)$$

$$\eta^{25}_{i+j}=\frac{d_i^2 d_j^2}{(w_i d_j+w_j d_i)^2}(1.2557w_i^2+1.6567w_j^2+2.1012w_i w_j) \cdots\cdots 18)$$

The emperical constants (α and β in Myer-Milius Equation, K' and K'' in Ishikawa-Baba Equation) were respectively determined by using the datas of observed viscosity according to the method of mathematical mean. In Ishikawa Equation, in spite of calculating the viscosity, we examined the constancy of the value K which was obtained by transforming the original equation into the next form ;

$$\frac{\eta_{i+j}-\eta_i}{\eta_j-\eta_{i+j}}\,\frac{1-z_m}{z_m}=\frac{k_j a_j}{k_i a_i}=K \quad\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \quad 19)$$

Table 4. The Certification of Myer-Milius Equation.
i ; Dioxane, j ; Cyclohexane
$\alpha\varphi_i=1.10757\varphi_i=0.85873$, $\beta\varphi_j=1.11172\varphi_j=1.14596$, 20°C

w_i	$\alpha\varphi_i w_i$	$\beta\varphi_j w_j$	$(\varphi_{i+j})_c$	$(\eta_{i+j})_c$	$(\eta_{i+j})_o$	△	△ %
0.00000	0.00000	1.14596	1.14596	0.87263	0.97012	−0.09749	10.0492
0.08618	0.07400	1.04720	1.12120	0.89190	0.93197	−0.04007	4.2994
0.16143	0.13862	0.96096	1.09958	0.90943	0.91551	−0.00608	0.6641
0.23329	0.20033	0.87861	1.07894	0.92683	0.90777	+0.01906	2.0996
0.30266	0.25990	0.79912	1.05902	0.94426	0.90906	+0.03520	3.8721
0.36956	0.31735	0.72245	1.03980	0.96172	0.91655	+0.04517	4.9282
0.45625	0.39179	0.62311	1.01490	0.98531	0.93397	+0.05134	5.4969
0.53749	0.46155	0.53001	0.99156	1.00851	0.95754	+0.05097	5.3230
0.61384	0.52712	0.44252	0.96964	1.03131	0.98596	+0.04535	4.5995
0.68933	0.59194	0.35601	0.94795	1.05490	1.02131	+0.03359	3.2889
0.76939	0.66069	0.26426	0.92495	1.08113	1.06922	+0.01191	1.1128
0.84331	0.72417	0.17956	0.90373	1.10652	1.12379	−0.01727	1.5367
0.91126	0.78252	0.10169	0.88421	1.13095	1.18669	−0.05574	4.6970
1.00000	0.85873	0.00000	0.85873	1.16451	1.28977	−0.12526	9.7118

* These certifications were performed according to Eq. 15.

Table 5. The Certification of Ishikawa Equation.
i ; Dioxane, j ; Cyclohexane, 20°C.

$(z_m)_i$	$(z_m)_j$	η_{i+j}	$(1-z_m)/z_m$	$\eta_j-\eta_{i+j}$	$\eta_{i+j}-\eta_i$	$\frac{\eta_{i+j}-\eta_i}{\eta_j-\eta_{i+j}}$	K
0.00000	1.00000	0.97012					
0.08259	0.91741	0.93197	0.09002	+0.03815	−0.35780	− 9.37876	− 0.8442
0.15532	0.84468	0.91551	0.18388	+0.05461	−0.37426	− 6.85332	− 1.2602
0.22515	0.77485	0.90777	0.29057	+0.06235	−0.38200	− 6.12670	− 1.7802
0.29304	0.70696	0.90906	0.41450	+0.06106	−0.38071	− 6.23501	− 2.5844
0.35891	0.64109	0.91655	0.55984	+0.05357	−0.37322	− 6.96695	− 3.9003
0.44491	0.55509	0.93397	0.80150	+0.03615	−0.35580	− 9.84232	− 7.8886
0.52606	0.47394	0.95754	1.10997	+0.01258	−0.33223	−26.4093	−29.313
0.60293	0.39707	0.98596	1.51844	−0.01584	−0.30381	+19.1799	+29.1235
0.67943	0.32057	1.02131	2.11944	−0.05119	−0.26846	+ 5.24438	+11.115
0.76117	0.23883	1.06922	3.18707	−0.09910	−0.22055	+ 2.22552	+ 7.0928
0.83717	0.16283	1.12379	5.14137	−0.15367	−0.16598	+ 1.08010	+ 5.5531
0.90749	0.09251	1.18669	9.80964	−0.21657	−0.10308	+ 0.47596	+ 4.6689
1.00000	0.00000	1.28977					

* These certifications were performed according to Eq. 19.

Table 6. The Certification of Ishikawa-Baba Equation.
i ; Dioxane, j ; Cyclohexane, 20°C.
$K'=1.4167$, $K''=1.4092$, $\eta_i=1.28977$, $\eta_j=0.97012$

$(z_m)_j$	$1+K'\frac{z_m}{1-z_m}$	$\frac{\eta_i}{1+K'\frac{z_m}{1-z_m}}$	$1+K''\frac{1-z_m}{z_m}$	$\frac{\eta_j}{1+K''\frac{1-z_m}{z_m}}$	$(\eta_{i+j})_c$	$(\eta_{i+j})_o$	△ %
1.00000						0.97012	
0.91741	16.7367	0.07706	1.12685	0.86091	0.93797	0.93197	0.6437
0.84468	8.70446	0.14817	1.25912	0.77047	0.91864	0.91551	0.3418
0.77485	5.87554	0.21951	1.40947	0.68828	0.90779	0.90777	0.0022
0.70696	4.41778	0.29194	1.58411	0.61240	0.90434	0.90906	0.5192
0.64109	3.53052	0.36532	1.78892	0.54229	0.90761	0.91655	0.9753
0.55509	2.76753	0.46603	2.12947	0.45556	0.92159	0.93397	1.3255
0.47394	2.27633	0.56660	2.56416	0.37833	0.94493	0.95754	1.3169
0.39707	1.93298	0.66724	3.13978	0.30897	0.97621	0.98596	0.9888
0.32057	1.66842	0.77304	3.98671	0.24333	1.01637	1.02131	0.4836
0.23883	1.44450	0.89288	5.49121	0.17666	1.06954	1.06922	0.0299
0.16283	1.27554	1.01115	8.24521	0.11765	1.12880	1.12379	0.4458
0.09251	1.14441	1.12701	14.8237	0.06544	1.19245	1.18669	0.4853
0.00000						1.28977	

* These certifications were performed according to Eq. 16.

Table 7. The Certification of Takano Equation.
i ; Dioxane, j ; Cyclohexane, 20°C.
$M_i=88.11$ $M_j=84.16$
$d_i=1.03504$ $d_j=0.77957$
$\eta_{ii}=1.28977$ $\eta_{jj}=0.97012$
$\lambda=0.93344$, $\mu=1.64549$, $\nu=2.09439$

w_i	$(z_m)_j$	A **	B	$(\eta_{i+j})_c$	$(\eta_{i+j})_o$	△	△ %
0.00000	1.00000	0.60771	1.59632	0.97009	0.97012	−0.00003	0.0030
0.08618	0.91741	0.63442	1.49855	0.95056	0.93197	+0.01859	1.9946
0.16143	0.84468	0.65921	1.42306	0.93796	0.91551	+0.02245	2.4521
0.23329	0.77485	0.68426	1.35957	0.93029	0.90777	+0.02252	2.4808
0.30266	0.70696	0.70982	1.30621	0.92717	0.90906	+0.01811	1.9921
0.36956	0.64109	0.73584	1.26216	0.92874	0.91655	+0.01219	1.3299
0.45625	0.55509	0.77177	1.21589	0.93838	0.93397	+0.00441	0.4721
0.53749	0.47394	0.80785	1.18361	0.95617	0.95754	−0.00137	0.1430
0.61384	0.39707	0.14412	1.16302	0.98172	0.98596	−0.00424	0.4300
0.68933	0.32057	0.88246	1.15198	1.01657	1.02131	−0.00474	0.4641
0.76939	0.23883	0.92604	1.15038	1.06529	1.06922	−0.00393	0.3675
0.84331	0.16283	0.96922	1.15812	1.12247	1.12379	−0.00132	0.1174
0.91126	0.09251	1.01162	1.17307	1.18670	1.18669	+0.00001	0.0008
1.00000	0.00000	1.07129	1.20392	1.28974	1.28977	−0.00003	0.0023

* These certifications were performed according to Eq. 17.

** $A=d_i^2 \times d_j^2 / (w_i d_j + w_j d_i)^2$

$B=\lambda w_i^2 \eta_{ii} + \mu w_j^2 \eta_{jj} + \nu w_i w_j \eta_{ij}$, the value of η_{ij} was obtained from that of the equimolar composition.

In the case of Takano Equation, without containing such emperical constants as related to the nature of the system, the calculations of the viscosity were performed directly from the corresponding datas of the pure solvents i and j at 20°C and 25°C.

Table 8. The Certification of Takano Equation.
i ; Dioxane, j ; Cyclohexane, 25°C.
$M_i=88.11$ $M_j=84.16$
$d_i=1.02971$ $d_j=0.77699$
$\eta_{ii}=1.33145$ $\eta_{jj}=1.00019$
$\lambda=0.94312$, $\mu=1.65642$, $\nu=2.13110$.

w_i	$(z_m)_j$	A **	B	$(\eta_{i+j})_c$	$(\eta_{i+j})_o$	△	△ %
0.00000	1.00000	0.60370	1.65673	1.00016	1.00019	−0.00003	−0.0029
0.08697	0.91667	0.63034	1.55741	0.98169	0.96581	+0.01588	+1.6442
0.23429	0.77382	0.67963	1.41721	0.96317	0.94288	+0.02029	+2.1519
0.36305	0.64749	0.72760	1.32352	0.96299	0.95135	+0.01164	+1.2235
0.42948	0.58174	0.75435	1.28570	0.96986	0.96396	+0.00590	+0.6120
0.48728	0.52419	0.77886	1.25862	0.98028	0.97894	+0.00134	+0.1368
0.54568	0.46573	0.80488	1.23676	0.99544	0.99722	−0.00178	0.1784
0.59764	0.41342	0.82909	1.22196	1.01311	1.01702	−0.00391	0.3844
0.65262	0.35784	0.85596	1.21107	1.03662	1.04209	−0.00547	0.5249
0.75632	0.25220	0.91030	1.20389	1.09590	1.10090	−0.00500	0.4541
0.85435	0.15140	0.96656	1.21313	1.17256	1.17467	−0.00211	0.1796
0.94934	0.05289	1.02622	1.23697	1.26940	1.26924	+0.00016	+0.0126
1.00000	0.00000	1.06029	1.25571	1.33141	1.33139	+0.00002	+0.0015

* These certifications were performed according to Eq. 18.

** $A=d_i^2\,d_j^2\,/\,(w_id_j+w_jd_i)^2$

$B=\lambda w_i^2\,\eta_{ii}+\mu w_j^2\,\eta_{jj}+\nu w_iw_j\eta_{ij}$, the value of η_{ij} was obtained from that of the equimolar composition.

IV. DISCUSSION

It is very important through these investigations to clear out whether the mixed solvent used gives or not the nature of ideal mixture. The elucidations of this problem were performed from the two different ways i.e., the measurement of density and the measurement of dieclectric constant. The observed densities of this system showed good identity with the calculated ones according to the Eq. 3) which were deduced from the idea of ideal mixture as shown in Table 1. This fact shows us that the nature of this mixed solvent system is likely that of ideal mixture. The another certification was undertaken by the use of dielectric measurements. As already reported in the former papers, the dielectric constants of mixed solvents of i and j components are expressed by the following equation if the system is ideal mixture[9] ;

$$1/\varepsilon_{i+j}=w_id_j/(w_id_j+w_jd_i)\,\varepsilon_i+w_jd_i/(w_id_j+w_jd_i)\,\varepsilon_j\cdots\cdots\cdots\cdots\cdots \quad 20)$$

where d_i end d_j are the densities, ε_i and ε_j are the dielectric constants of pure solvents i and j respectively. Table 9 shows an example of the result of dielectric observation on the dioxane-cyclohexane system at 25°C by using the sinsoidal wave of 10 c/s. As clearly shown in this table, the dielectric constants observed exhibited good identity with the calculated ones.

Table 9. The Dielectric Constant of Dioxane-Cyclohexane System.
i ; Dioxane, j ; Cyclohexane, 25°C, 10c/s.
$d_i=1.02971$, $d_j=0.77699$
$\varepsilon_i=2.2397$, $\varepsilon_j=2.0365$

w_i	A **	B	$A+B$	$(\varepsilon_{i+j})_c$*	$(\varepsilon_{i+j})_o$	△	△ %
1.00000	0.44648	0.00000	0.44648	2.2397	2.2397	0.0000	0.0000
0.94934	0.41700	0.03243	0.44948	2.2250	2.2272	0.0023	0.0987
0.85435	0.36420	0.09049	0.45469	2.1993	2.1996	0.0003	0.0136
0.63752	0.31289	0.14692	0.45981	2.1748	2.1699	0.0049	0.2258
0.70351	0.28648	0.17596	0.46244	2.1624	2.1566	0.0058	0.2689
0.65262	0.26180	0.20311	0.46491	2.1509	2.1439	0.0070	0.3265
0.59764	0.23598	0.23153	0.46748	2.1390	2.1330	0.0060	0.2812
0.54568	0.21227	0.25758	0.46985	2.1283	2.1188	0.0095	0.4483
0.48728	0.18646	0.28596	0.47242	2.1167	2.1104	0.0063	0.2985
0.42948	0.16174	0.31315	0.47489	2.1057	2.0992	0.0065	0.3096
0.30365	0.13427	0.34336	0.47763	2.0936	2.0854	0.0082	0.3932
0.23429	0.08375	0.39893	0.48268	2.0717	2.0664	0.0053	0.2564
0.08697	0.02993	0.45811	0.48804	2.0490	2.0485	0.0005	0.0244
0.00000	0.00000	0.49103	0.49103	2.0365	2.0365	0.0000	0.0000

* These values of $(\varepsilon_{i+j})_c$ were calculated according to Eq. 20).
** These values A and B were calculated respectively from ;
$A=w_i d_j/\varepsilon_i(w_i d_j+w_j d_i)$
$B=w_j d_i/\varepsilon_j(w_i d_j+w_j d_i)$

Considering from these experimental results, we can draw a reliable conclusion on the nature of the system that it can be recognized as an ideal mixture. Under the above mentioned nature of the system, it will be naturally expected that Myer-Milius Equation and also Takano Eqation, which were all derived from the same assumption in which the specific volume satisfy the additivity law as expressed in Eq. 3), must show at least the same degree of identity for the system of ideal mixture as it was used in these investigations if the other assumptions taken are correct.

In the case of Ishikawa Equation, although it was derived from the different assumption that the molecules of the mixed solvent make a molecular cluster by association, it seems to be deduced from the same idea as already mentioned if the assumption of the additivity rule on the viscosity is excluded.

Accordingly, it can be presumably expected that Myer-Milius Equation, Takano Equation and also Ishikawa Equation are naturally attributed to the idea of ideal mixture and the results calculated according to these equations will give fairly good identities to the observed ones. However, the experiments showed an undesirable results excepting the case of Takano Equation. The results of the identity test for Myer-Milius Equation were very unsatisfactory as shown in Table 4 and the maximum error reached over ten percent. Likely to the above results, Ishikawa Equation also exhibited more undesirable results with a maximum error of 29 percent in the constant K, as illustrated in Table 5.

The theoretical base of Takano Equation is concerned with, as already shown in the theoretical part of this paper, the idea that the internal restrictive forces depend merely upon the molecular interaction of dipole-dipole or atom-dipole interaction as Debye proposed. These ideas naturally lead the conclusion that the viscosity of a solvent mixture can be descrived by the probability of the penetration of moving molecules into the small limitted active space. Thus, in the viscosity equation, although the idea of non-ideal mixture was taken into it in the form of mutual interaction of dipole molecules, this equation contains in it an assumption of ideal mixture in the following two points ; (1) As laready shown in the original paper, the constant K_{ii}, K_{jj} and K_{ij} in Eq. 12) were determined theoretically in applying the initial conditions of the pure solvents i and j. These treatments mean the introduction of indifferent quantities from the mutual interaction into the equation and characterized it as an equation for ideal mixture. (2) The most remarkable nature of this eqnation is the fact that this equation was derived by introducing the law of additivity for specific volume in the form of Eq. 3). Accordingly, it is very natual that this equation showed a good identity to the observed results. We must remember here that all values of densities used in these calculations of viscosities were all obtained, as shown in Tables 2 and 3, not given by the direct observations, by applying the calculated ones according to Eq. 3 which was deduced from the assumption of ideal mixture. And this fact of good identity deservedly shows that the system used in our investigations is almost ideal mixture as it has already been proved by the dielectric measurements.

Considering these experimental premises, the fact that Ishikawa-Baba Equation showed good identity is rather inquirous. As already mentioned in the theoretical part of this paper, this equation was derived by assuming the association of molecules, and this idea is expressed in the physical meanning of the constants K' and K''. However, it seems to be merely formal, and if the idea of association is exactly taken into account, these constants K' and K'' can not be 'constant'.

In conclusion, Ishikawa-Baba Equation must be refined by transforming these constants K' and K'' into some function of Z.

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