

STUDIES ON THE DIELECTRIC PROPERTIES OF ORGANIC SOLVENTS (I)

Part 1.

Dielectric Dispersion in Ultra Low Frequency (1)

By

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1. Introduction

The dielectric dispersion in high frequency range have already been studied by P. Debye ¹⁾, M. Gevers ²⁾, R. G. Breckenridge ³⁾ W. Shotkley ⁴⁾ and others ⁵⁾. Debye had first introduced a theory that the dielectric constant in alternating field is generally expressed as a function of the frequency used, and is also expressed as a complex quantity owing to the presence of the internal friction between the dipole molecules in the alternating field, i. e

$$\varepsilon = \varepsilon' - j\varepsilon'' \dots \dots \dots 1)$$

where $j^2 = -1$, and

$$\varepsilon' = \varepsilon_{ea} + \frac{\varepsilon_s - \varepsilon_{ea}}{1 + \omega^2 \tau^2} \dots \dots \dots 2)$$

$$\varepsilon'' = (\varepsilon_s - \varepsilon_{ea}) \frac{\omega \tau}{1 + \omega^2 \tau^2} \dots \dots \dots 3)$$

In Eqs. 2 and 3, ε_s represents the dielectric constant in the static field and ε_{ea} is a dielectric constant due to atomic and electronic polarization, ω the angular velocity at frequency ν , τ the relaxation time. The real part of the dielectric constant ε' in Eq. 1 shows the ordinal dielectric constant due to the pure polarization, and this value decreases with increasing frequency. The second term, deduced from the lag of the phase angle, shows practically the dielectric loss due to the internal friction of the dipole molecules in the alternating field. By differentiating the both terms of Eq. 3, we can easily deduce the following conclusion that the absolute value of the imaginary part of the complex dielectric constant has a maximum value when $\omega\tau=1$. As clearly shown in Eq. 2, the real part of the dielectric constant decreases suddenly in the vicinity of the frequency at $\omega\tau=1$. The above mentioned theory is actually proved in many organic dielectrics. Generally speaking, the fact that the dielectric constant observed in the alternating field varies with the frequency has been described in terms of dispersion.

In recent times, the studies of the dielectric properties of the various organic substances have been extended their trend of research not only to the analysis of the molecular structure but also to their application for electrical technics. The dielectric loss angle which is expressed by the ratio of the two dielectric constants ε' and ε'' , has also been considered to be the most interesting subject on the electrical properties in solid state physics especially in high polymer substances.

In this paper, the dispersion of the dielectric constants in very low frequency below ten cycles per second has been investigated on the some organic substances such as dioxane or benzene.

2. Experimental

The apparatus used in this experiment was T. R-4 type dielectric analyser in ultra low frequency made of Ando Electric Company. The oscillator used was Andos' U. L. 0-1 type of ultra low frequency oscillator and which can supply sinsoidal, triangle and squire wave successbily within the range from 0.01 to 100 cycles per second. The schematic diagram of the full arrangements is shown in Fig. 1. The oscillator and the detector were strictly protected from the voltage variation of the input power supply by using the voltage stabilizer. The detector, E. D. C-3 type of high sensitive unbalance detector, is very sensitive for the change of the external field and this made impossible to detect the balancing point especially in very low frequency. To avoid these difficulties, the special precautions were employed for the arrangements of the full appatatus. The cell used was Andos' L. E-3 type cell for liquid use. Exaetly the 7 c. c of sample was taken by pipet into the cell and incubated in the air thermostat. The temperature of the thermostat was exactly controlled at the accuracy of $\pm 0.05^\circ\text{C}$ by the use of mercury regulator and vacume tube relay. The treatment of packing sample into the cell was undertaken in the dry air stream in avoiding the absorption of air moisture. This process is very important for the precise measurements of the dielectric constants especially in the case of water absorptive substances. Fig. 2-a shows the variation of the dielectric constant of dioxane due to such moisture absorption. Fig. 2-b shows the results of avoiding moisture by taking the cell into the thermostat in which the completely dried air stream was introduced.

Such preliminary tests were carried out befor all measurements in order to check the moisture absorption. The other important problem for the precise measurements is to check the constancy of the cell constant through all ranges of the frequency used. Fig. 3 shows the results of such examinations. As clearly shown in this figure, the cell constant remains almost constant in all ranges of the frequency used.

3. Results of the Experiments

Fig. 4 shows the dielectric dispersion of the real part of the dielectric constants of pure dioxane at 30° , 35° and 40°C respectively. Figs. 5, 6 and 7 show the same results with the comparison of the imaginary part of the dielectric constants, $\tan \delta$, and the conductance at every temperature. Figs. 8 and 9 are the results of benzene at 30°C . Through these experiments, the moisture absorption into the sample and the variation of the cell constant are strictly pre-examined by the method mentioned above.

Fig. 1. Schematic Diagram of Apparatus.

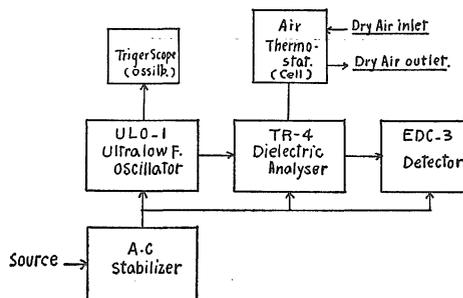


Fig. 2. Water Absorption of Dioxane (1c/s).

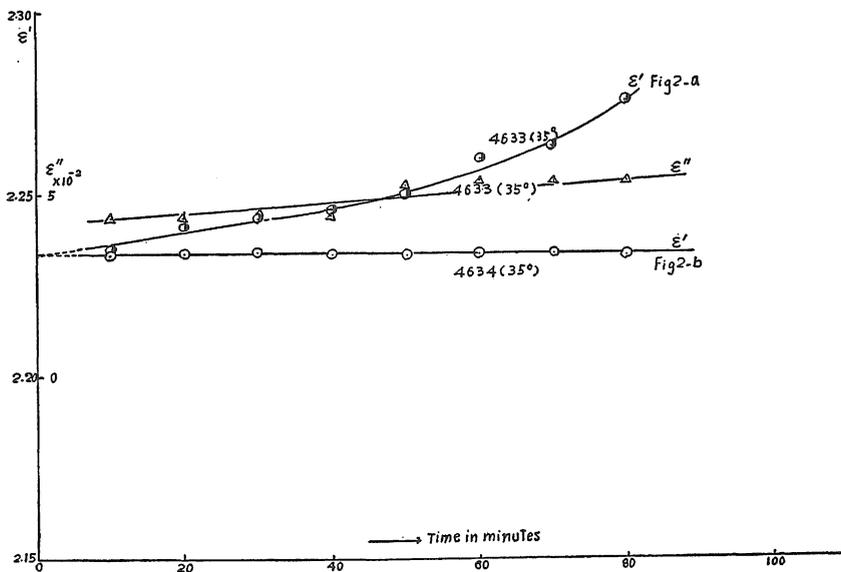


Fig. 3. The Effect of Frequency on the Cell Constant (30°C ± 0.05°).

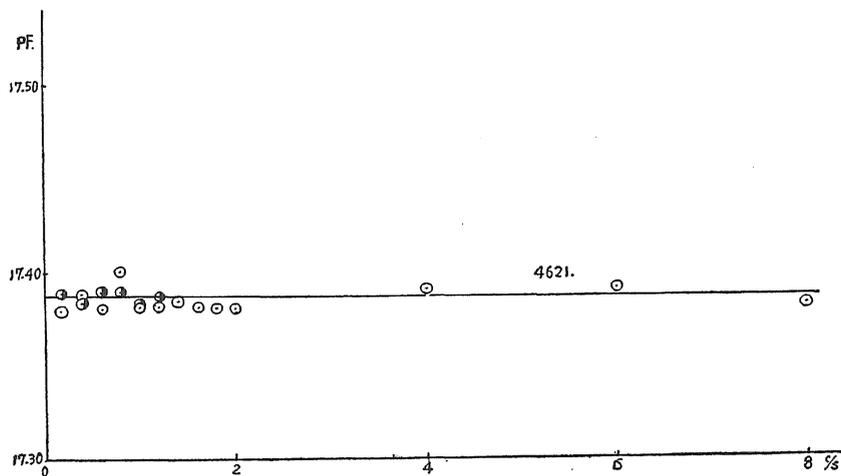


Fig. 4. Dielectric Dispersion of Dioxane.

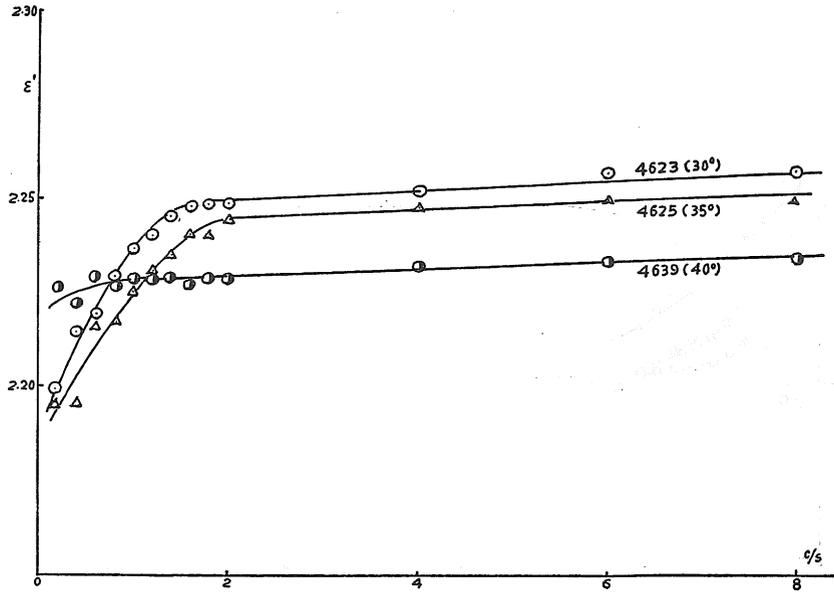


Fig. 5. Dielectric Dispersion of Dioxane
(4623, 30°C ± 0.05°).

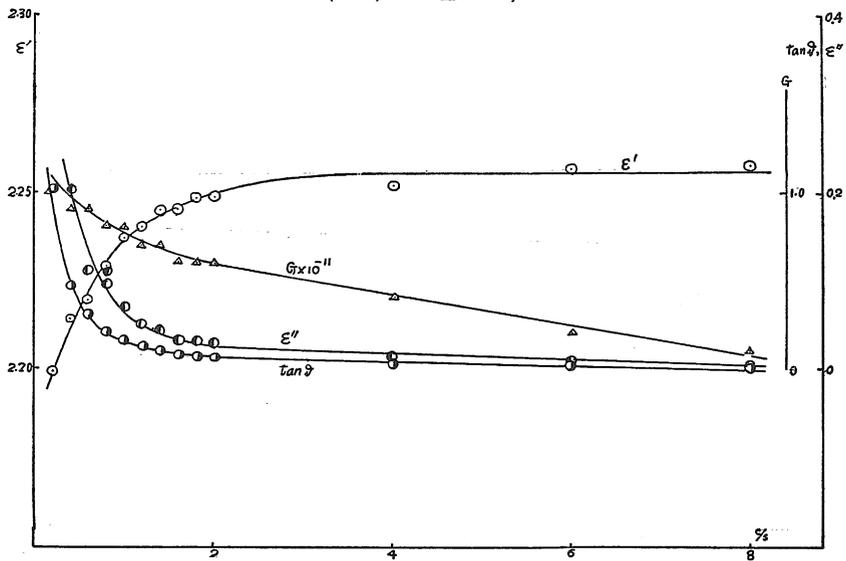


Fig. 6. Dielectric Dispersion of Dioxane.
(4625, 35°C ± 0.05°)

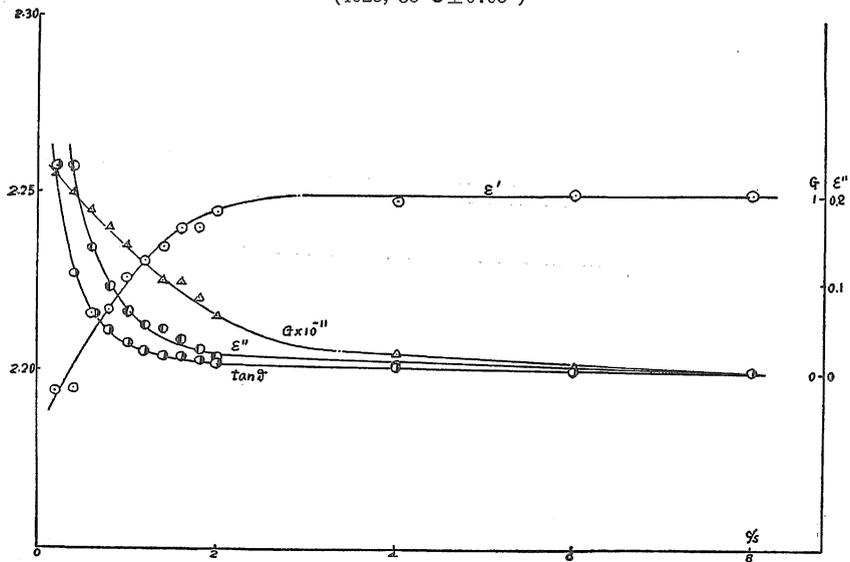


Fig. 7. Dielectric Dispersion of Dioxane.
(4639, 40°C ± 0.05°)

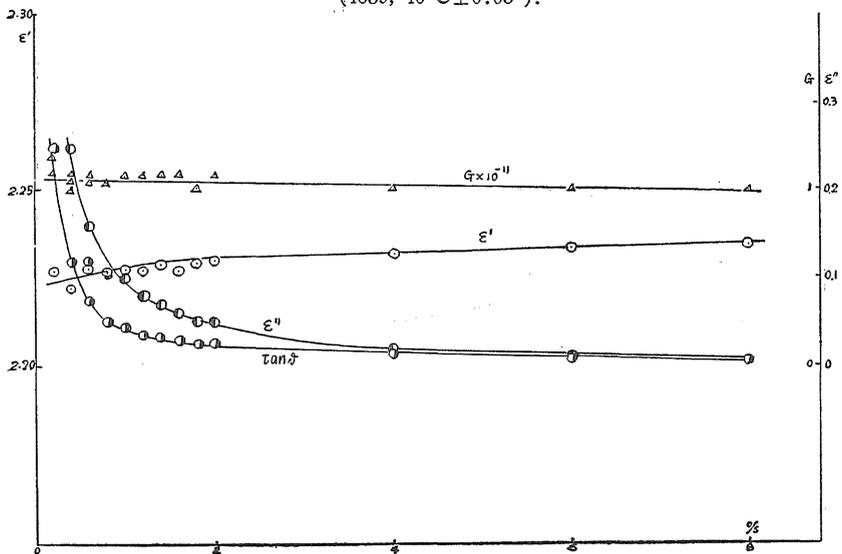


Fig. 8. Dielectric Dispersion of Benzene
(4631, 4632, $30^{\circ}\text{C} \pm 0.05^{\circ}$).

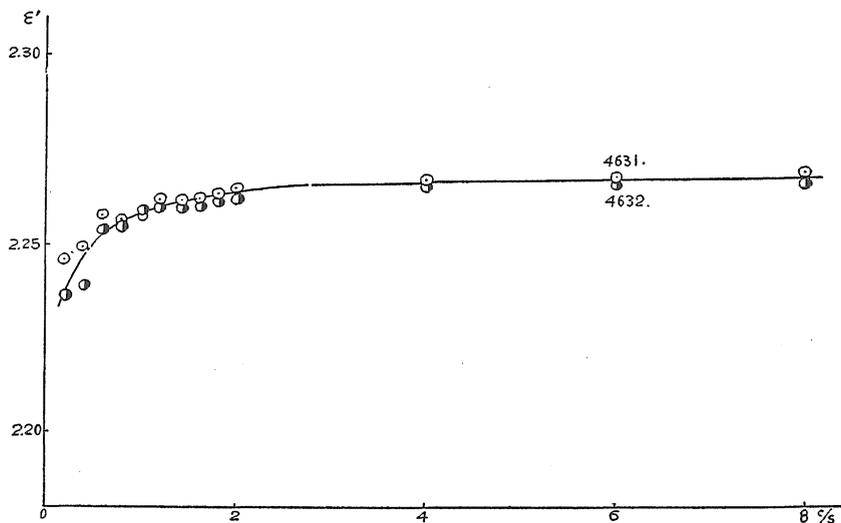
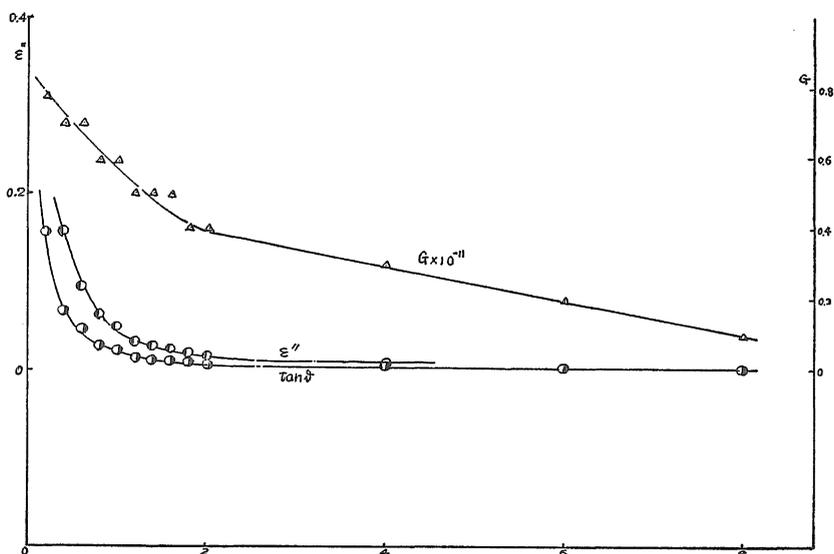


Fig. 9. Dielectric Dispersion of Benzene
(4631, $30^{\circ}\text{C} \pm 0.05^{\circ}$).



4. Discussion

All the results obtained in dioxane show remarkable depression of the real part of the dielectric constants in the frequency below two cycles per second. These depressions of the dielectric constants can also be recognized in the case of benzene as same as in the case of dioxane.

In comparison of the data obtained in dioxane at various temperature, it seems likely that these depression of the real part of the dielectric constantt has some connection with the temperature. For instance, the effect of the temperature upon the depression of the real part of the dielectric constant is considerably weaken at the temperature of 40°C. In connected with the depression of the real part of the dielectric constants, all results show the remarkable increase in conductance G , $\tan \vartheta$, and ε'' with decreasing frequency. In conclusion, these results are clearly in contradiction with the expectations that derived from the Debye theory, i. e, the real part of the dielectric constants must increase with the decreasing frequency and it must reach to a fixt value ε_s as mentioned first. The same contradiction can also be recognized in the imaginary part of the dielectric constants and also in $\tan \vartheta$.

Accordingly, the results obtained through these experiments ⁶⁾ show us that the dispersion in ultra low frequency below two cycles per second would be related to some other causes which are theoretically different from the Debye dispersion.

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STUDIES ON THE DIELECTRIC PROPERTIES OF ORGANIC SOLVENTS (I)

Part 2.

A New Equation on the Dielectric Constant of Binary Organic Solvent Mixtures

1. Introduction

It has been well known that the dielectric constant of a binary solvent mixture can ordinarily be calculated by combination of Clausius-Mosotti relation ¹⁾ and the additivity law concerning the molecular polarizations of the pure components. But the Clausius-Mosotti relation is applicable only to the non-polar solvent and less satisfactorily to the ordinary polar solvent owing to the effect of the molecular association between the two interacting molecules

Thus, the Clausius-Mosotti equation is not generally usable for calculating the dielectric constant of a mixture even in the case when one of the substances is polar. An attempt to calculate the dielectric constant of such mixed solvents necessarily leads us to expressing the molecular interactions in terms of dielectric constant as closely as possible. One of such approach is to modify the Clausius-Mosotti formula by supplementing an adequate compensation term due to the molecular interactions. H. Müller ²⁾ seems to be the first person who drew notice to this problem, he postulated some formulas of this type when he tried to explain the remarkable difference in the dielectric constant between liquid and gas. Onsager ³⁾ abandoned the Clausius-Mosotti equation and postulated the idea that the mean orientation of a molecule is determined by the force couple exerted by a spherical-cavity field which is given by the shape of the molecule and which is proportional to the external field. From these premises ⁴⁻⁶⁾ he deduced an equation including the dielectric constant of the pure polar liquids. Later, Kirkwood ⁷⁾ modified Onsager equation by taking account of a new parameter concerning the molecular association. On the other trends of these investigations ⁸⁾, a comparative studies on the difference of the molecular polarizations of liquids and gases were undertaken in relation to the Van der Waals equation of a non-ideal gas.

Keesom ⁹⁾ for the first time estimated the average interaction energy between the two molecules of a non ideal gas as the energy of electrostatic force acting between two dipole molecules. Keesom's energy is thus considered to be a pure dipole-dipole interaction energy, and his theory may be applied to estimating the dielectric constant of mixtures under our considerations ^{10), 11)}.

In this paper, on the basis of Keesom's theory, a theoretical equation applicable to an ordinary polar-liquid mixture of organic substances is derived, in a way different from Clausius-Mosotti's derivation, as a result of analyzing the energy relations on a given electric displacement in a polarized liquid. At the end, the conformity of the

calculated values from the new equation with the observed values is pre-examined on the various kinds of organic binary solvent mixtures.

2. Theoretical

Let us consider a system of a binary solvent mixture containing pure components i and j that have no mutual electrostatic interaction. The unit volume of this mixture contains respectively v_i and v_j cc of i and j component, then $v_i + v_j = 1$. On the other hand, according to the electrostatic theory of dielectrics, the electrostatic energies stored in these small volume elements are respectively expressible by $v_i D^2/8\pi\epsilon_i$, and $v_j D^2/8\pi\epsilon_j$ at a given electric displacement D , where ϵ_i and ϵ_j denote the dielectric constants. Thus, denoting the dielectric constant of the mixture as ϵ_{i+j} , we have (cf. Appendix 1) :

$$\frac{D^2}{8\pi\epsilon_{i+j}} = \frac{v_i D^2}{8\pi\epsilon_i} + \frac{v_j D^2}{8\pi\epsilon_j} \dots\dots\dots 1)$$

Further, using weight fractions w_i and w_j instead of v_i and v_j and dividing every term of Eq. 1 with $D^2/8\pi$, we have

$$\frac{1}{\epsilon_{i+j}} = \frac{w_i d_j}{\epsilon_i (w_i d_j + w_j d_i)} + \frac{w_j d_i}{\epsilon_j (w_i d_j + w_j d_i)} \dots\dots\dots 2)$$

Here, d_i and d_j denote the densities.

The above equation 2 shows the effective dielectric constant of the binary solvent mixture in the ideal case when the two kinds of molecules of the mixture have no mutual interaction. But in the real cases, owing to the presence of mutual interaction, the above equation does not hold. Then we assume that such molecular interaction is attributable only to the dipole-dipole interaction. On this assumption, Eq. 1 must be modified by addition of a term U_{ij} that represents energy released when the interacting molecules change their orientations in the dipole field, and we have

$$\frac{D^2}{8\pi\epsilon_{i+j}} = \frac{v_i D^2}{8\pi\epsilon_i} + \frac{v_j D^2}{8\pi\epsilon_j} - U_{ij} \dots\dots\dots 3)$$

Applying Keesom theory, and taking into account the number of molecules effectively interacting, we have

$$U_{ij} = \frac{D^2}{8\pi\epsilon_{ij}} = \frac{2\mu_i^2 \mu_j^2}{3r_{ij}^6 kT} f_i f_j n_{ij} \dots\dots\dots 4)$$

where ϵ_{ij} represents the equivalent dielectric constant due to the dipole-dipole interaction, r_{ij} the mean effective distance between the interacting molecules, μ_i or μ_j the dipole moments, f_i or f_j the mol fraction, and n_{ij} the total number of the interacting molecules in the unit space. N , M , and d respectively denote the Avogadro number, molecular weight, and density. The values of f_i , f_j and n_{ij} are calculated as follows ;

$$\left. \begin{aligned} f_i &= \frac{w_i M_j}{w_i M_j + w_j M_i} \\ f_j &= \frac{w_j M_i}{w_i M_j + w_j M_i} \\ n_{ij} &= \frac{d_i d_j (w_i M_j + w_j M_i) N}{M_i M_j (w_i d_j + w_j d_i)} \end{aligned} \right\} \dots\dots\dots 5)$$

Combining Eqs. 3, 4 and 5, and dividing every term of the resulting equation by $D^2/8\pi$, we have

$$\frac{1}{\epsilon_{i+j}} = \frac{w_i d_j}{\epsilon_i (w_i d_j + w_j d_i)} + \frac{w_j d_i}{\epsilon_j (w_i d_j + w_j d_i)} - \frac{\beta w_i w_j}{(w_i M_j + w_j M_i)(w_i d_j + w_j d_i)} \dots 6)$$

with

$$\beta = \frac{16\pi N\mu_i^2 \mu_j^2 d_i d_j}{3D^2 r_{ij}^6 kT} \dots 7)$$

Since it is generally difficult to determine the value of r_{ij} from pure theory, we determine the quantity instead of r_{ij} , from observed values of the dielectric constants in the case where $w_i = w_j$ by use of an empirical equation

$$\beta = (M_i + M_j)(d_i + d_j) \left\{ \frac{d_j}{\epsilon_i (d_i + d_j)} + \frac{d_i}{\epsilon_j (d_i + d_j)} - \frac{1}{(\epsilon_{i+j})_{i=j}} \right\} \dots 8)$$

and expect that the quantity β would be approximately constant independent of change in composition.

Eq. 6 has now been proved well applicable to materials with low dipole moments, and the agreement of the calculated values with the observed values is far better than in the case of Clausius-Mosotti equation or Kirkwood equation. The average errors $\bar{\Delta}$ in the full rauges of j are below one percent in such materials.

The following table draw some examples of calculating the dielectric constants according to Eq.6 with 8 on various kinds of organic binary mixtures, and show how this theory conforms with experiment.

TABLE 1.

	M_i	M_j	d_i	d_j	μ_i	μ_j	$\bar{\Delta}(\%)$
H ₂ O-C ₂ H ₅ OH	18.01	46.07	0.998	0.789	2.50	1.67	0.509
C ₆ H ₆ -Dioxane	78.11	88.10	0.878	1.032	0	0.43	0.056
CCl ₄ -CS ₂	153.84	76.14	1.592	1.263	0	0	0.043
CCl ₄ -C ₆ H ₆	153.84	78.11	1.592	0.878	0	0	0.230
C ₂ H ₅ -O-C ₂ H ₅ -C ₆ H ₆	74.12	78.11	0.719	0.878	1.22	0	0.202
H ₂ O-Dioxane	18.01	88.10	0.998	1.032	2.50	0.43	0.774
H ₂ O-CH ₃ OH	18.01	32.04	0.998	0.792	2.50	1.69	1.020
CS ₂ -C ₆ H ₅ Br	76.14	157.02	1.263	1.495	0	1.48	0.897
C ₂ H ₅ O-C ₂ H ₅ -C ₅ H ₁₂	74.12	72.15	0.719	0.626	1.22	0	1.239
C ₆ H ₅ NH ₂ -mXylene	93.12	106.16	1.022	0.864	0.37	0.99	1.690
CHCl ₃ -EAE	119.39	116.20	1.498	0.763	1.05	1.15	1.392
CHCl ₃ -C ₆ H ₆	119.39	78.11	1.498	0.878	1.05	0	1.213
CHCl ₃ -(C ₂ H ₅) ₂ O	119.39	74.12	1.498	0.719	1.05	1.22	1.893
CCl ₄ -C ₂ H ₅ OH	153.84	46.07	1.595	0.789	0	1.67	4.911
H ₂ O-Acetone	18.01	58.08	0.998	0.795	2.50	2.20	0.845
C ₆ H ₅ NO ₂ -C ₆ H ₅ CH ₃	123.11	92.13	1.222	0.866	4.19	0.37	>10
C ₆ H ₅ NO ₂ -C ₆ H ₆	123.11	78.11	1.222	0.878	4.19	0	>10
Acetone-C ₆ H ₆	58.08	78.11	0.785	0.878	2.85	0	>10
CH ₃ OH-C ₆ H ₆	32.04	78.11	0.792	0.878	1.70	0	>10
C ₂ H ₅ OH-C ₆ H ₆	46.07	78.11	0.789	0.878	1.67	0	>10.

Appendix 1. - Another Derivation of Eq. 2.

Let the volume elements in a unit space be v_i and v_j , and let the electrostatic energies stored in these volume elements at a given electric displacement D be e_i

and e_j . These energies are distributed in proportion to the numbers of the particles n_i and n_j contained in v_i and v_j , then the following relations may be expected

$$\left. \begin{aligned} e_i &= k_i n_i \\ e_j &= k_j n_j \end{aligned} \right\} \dots\dots\dots 1)$$

where k_i and k_j are proportionality constants, and n_i and n_j respectively are given by

$$n_i = Nm_i / M_i, \quad n_j = Nm_j / M_j. \dots\dots\dots 2)$$

Here m_i or m_j is the mass of a component liquid in the volume element, M_i or M_j the molecular weight, and N the Avogadro number. On the other hand, the weight fraction w_i and w_j are given respectively as

$$\left. \begin{aligned} w_i &= \frac{m_i}{m_i + m_j} = \frac{m_i}{d_{i+j}} \\ w_j &= \frac{m_j}{m_i + m_j} = \frac{m_j}{d_{i+j}} \end{aligned} \right\} \dots\dots\dots 3)$$

with

$$w_i + w_j = 1$$

where d_{i+j} stands for $m_i + m_j$, because

$$d_{i+j} = m_{i+j} / v_{i+j} = (m_i + m_j) / (v_i + v_j) = m_i + m_j.$$

From Eqs. 1, 2 and 3, we have

$$\left. \begin{aligned} e_i &= Nw_i k_i d_{i+j} / M_i \\ e_j &= Nw_j k_j d_{i+j} / M_j \end{aligned} \right\} \dots\dots\dots 4)$$

At the limit $w_i, w_j \rightarrow 1$, Eq. 4 becomes

$$\lim_{w_i \rightarrow 1} e_i = Nk_i d_i / M_i = \frac{D^2}{8\pi\epsilon_i} \dots\dots\dots 5)$$

$$\lim_{w_j \rightarrow 1} e_j = Nk_j d_j / M_j = \frac{D^2}{8\pi\epsilon_j} \dots\dots\dots 6)$$

Further,

$$\left. \begin{aligned} \frac{k_i N}{M_i} &= \frac{D^2}{8\pi\epsilon_i d_i} \\ \frac{k_j N}{M_j} &= \frac{D^2}{8\pi\epsilon_j d_j} \end{aligned} \right\} \dots\dots\dots 7)$$

From Eqs. 4 and 7, we have

$$\left. \begin{aligned} e_i &= \frac{w_i d_{i+j} D^2}{8\pi\epsilon_i d_i} \\ e_j &= \frac{w_j d_{i+j} D^2}{8\pi\epsilon_j d_j} \end{aligned} \right\} \dots\dots\dots 8)$$

The density of the ideal mixed solvents, without mutual molecular interaction, is related to the densities by ¹²⁾

$$\frac{1}{d_{i+j}} = \frac{w_i}{d_i} + \frac{w_j}{d_j} \dots\dots\dots 9)$$

Thus, from Eqs. 8 and 9 we have

$$\left. \begin{aligned} e_i &= \frac{w_i D^2 d_j}{8\pi\epsilon_i (w_i d_j + w_j d_i)} \\ e_j &= \frac{w_j D^2 d_i}{8\pi\epsilon_j (w_i d_j + w_j d_i)} \end{aligned} \right\} \dots\dots\dots 10)$$

with

$$e_{i+j} = \frac{D^2}{8\pi\varepsilon_{i+j}} \dots\dots\dots 11)$$

Owing to the additivity of energy $e_{i+j} = e_i + e_j$ in this ideal case, Eqs. 10 and 11 combine into

$$\frac{D^2}{8\pi\varepsilon_{i+j}} = \frac{w_i D^2 d_j}{8\pi\varepsilon_i (w_i d_j + w_j d_i)} + \frac{w_j D^2 d_i}{8\pi\varepsilon_j (w_i d_j + w_j d_i)} \dots\dots\dots 12)$$

where ε_{i+j} is the dielectric constant of the mixture. Dividing every term of Eq. 12 with $D^2/8\pi$, we have

$$\frac{1}{\varepsilon_{i+j}} = \frac{w_i d_j \varepsilon_i}{(w_i d_j + w_j d_i)} + \frac{w_j d_i \varepsilon_j}{(w_i d_j + w_j d_i)} \dots\dots\dots 13)$$

Appendix 2. – Derivation of Eq. 9 of Appendix 1.

Let the volumes of liquids to be mixed be v_i and v_j and their mass be m_i and m_j (as denoted in Appendix 1), then the density of the mixed solvent can be denoted as

$$d_{j+i} = m_{i+j}/v_{i+j} = (m_i + m_j)/(v_i + v_j) \dots\dots\dots 1)$$

Owing to the common relation between density and volume, it becomes

$$d_{i+j} = (m_i + m_j) d_i d_j / (m_i d_j + m_j d_i) \dots\dots\dots 2)$$

On the other hand, the weight fractions w_i and w_j are defined as follows,

$$\left. \begin{aligned} w_i &= m_i / (m_i + m_j) \\ w_j &= m_j / (m_i + m_j) \end{aligned} \right\} \dots\dots\dots 3)$$

Eliminating m_i and m_j from Eqs. 2 and 3, we have

$$1/d_{i+j} = w_i / d_i + w_j / d_j \dots\dots\dots 4)$$

The errors in applying Eq. 4 to various kinds of organic solvent mixtures were known to be below one percent except in a few special cases.¹²⁾

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