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Dielectric Relaxation and Molecular Structure. II. Notes on Analysing Dielectric Data of Dilute Solutions

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Dielectric data from dilute solution studies consist of two slopes, a' and a'', as defined by $\varepsilon'=\varepsilon_1'+a'c_2$ and $\varepsilon''=a''c_2$. In this article it is shown that the Debye equations for dilute solutions can be described by the use of a' and a''. These equations are obtained by replacing dielectric constant and loss, ε' and ε'' in Debye's equations for polar liquids by a' and a''. As applications of these new equations based on a' and a'' following topics are discussed: Symth's a', a'' plot in the complex plane; Scaife's method of polarizability plot; the familiar loss tangent method originated by Debye for obtaining the relaxation time in solution; and Gopola Krishna's new method for the same purpose.

To avoid the much disputed ambiguity[1] concerning the internal field correction, the dielectric relaxation time of a polar molecule is preferrably measured in dilute solutions of a non-polar solvent. However, the theoretical basis of the dilute solution method has not been well established. For instance, Smyth and his co-workers[2] in Princeton obtain two slopes, a' and a'', for dilute solutions of a polar substance in a non-polar solvent and make a plot of a' and a'' in the complex plane instead of the ε' and ε'' plot for the pure liquid. This procedure was justified graphically, that is, by plotting the dielectric constants and losses of solutions in the complex plane they obtained semi-circles which differed in size according to the concentration of the solute but had exactly the same shape with the semi-circle obtained by the a' and a'' plot. This proof is suggestive but may be better replaced by a mathematical expression in order to have a wider application of the a', a'' plot.

Thirty years ago Debye[3] devised a method of evaluating the relaxation time from the tan ϑ values of dilute solutions. A number of researchers[4] have used the latter method since; however, it has not been made clear whether there is any correlation between the two methods, i. e., between the loss tangent method of Debye and the slope method by Smyth.

In this short article it is shown that by the use of two slopes, a' and a'', one can describe the equations of Debye for dielectric relaxation, and that the Smyth procedure of the a' and a'' plot can be examined from this result. Furthermore, the loss tangent method originated by Debye and also the new method proposed by Gopola Krishna[5] can be derived from the equations based on two slopes; and Scaife's method of the polarizability plot[6] will become equivalent to the dielectric constant plot for dilute solution if the two slopes are used in the analysis of dielectric data.

General Theory

With the use of complex dielectric constant, $\varepsilon^*=\varepsilon'-i\varepsilon''$, the complex polarizability $p(\omega)$ is defined by*

$$p(\omega) = p' - ip'' = \frac{\varepsilon^*-1}{\varepsilon^*+2} \tag{1}$$

Consider a dielectric system consisting of dilute solution of a polar substance in a non-polar solvent. If this system is provided with a single relaxation time τ which arises from the polar solute molecules, the dependence of $p(\omega)$ upon the angular frequency ω will be described by

$$p(\omega) = p(\infty) + \frac{p(0)-p(\infty)}{1+i\omega\tau} \tag{2}$$

where

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[1] C. P. Smyth, "Dielectric Behavior and Structure," McGraw Hill Book Co., New York (1955), Chapter 2; C. J. F. Böttcher, "Theory of Electric Polarisation," Elsevier Publishing Co., Amsterdam (1952), Chapter 6; R. H. Cole, *J. Chem. Phys.*, **43**, 637 (1965).

[2] A. D. Franklin, W. M. Heston, Jr., E. J. Hennelly and C. P. Smyth, *J. Am. Chem. Soc.*, **72**, 3447. W. F. Hasel, M. D. Magee, S. W. Tucker and S. Walker, *Tetrahedron*, **20**, 2137 (1964).

[3] P. Debye, *Physik. Z.* **35**, 101 (1934).

[4] W. Jackson and J. G. Powles, *Trans. Faraday Soc.*, **42A**, 101 (1946) and several papers in the same appendix; C. P. Smyth, loc. cit., p. 64; C. J. F. Böttcher loc. cit., p. 375.

[5] K. V. Gopola Krishna, *Trans. Faraday Soc.*, **53**, 767 (1957).

[6] B. K. P. Scaife, *Proc. Phys. Soc.*, **81**, 124 (1963).

* The molecular polarization $P(\omega)=p(\omega)M/d$, in which M is the average molecular weight and d is density, is frequently used instead. See Ref. 1, C. P. Smyth, p. 59, Eq. (2.37) and Ref. 1, C. J. F. Böttcher, p. 356, Eq. (10.44).

$$\left.\begin{aligned} p(\infty) &= \frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2} \\ p(0) &= \frac{\varepsilon_0 - 1}{\varepsilon_0 + 2} \end{aligned}\right\} \tag{3}$$

in which ε_0 is the static dielectric constant and ε_∞ is the dielectric constant measured at frequencies so high that the permanent dipoles are unable to rotate. Since both ε_0 and ε_∞ are real, $p(0)$ and $p(\infty)$ are both real quantities while $p(\omega)$ has the real and the imaginary parts which are given by

$$\left.\begin{aligned} p' &= \frac{(\varepsilon'-1)(\varepsilon'+2)+\varepsilon''^2}{(\varepsilon'+2)^2+\varepsilon''^2} \\ p'' &= \frac{3\varepsilon''}{(\varepsilon'+2)^2+\varepsilon''^2} \end{aligned}\right\} \tag{4}$$

And from Eq. 2

$$\frac{(p'-ip'')-p(\infty)}{p(0)-p(\infty)} = \frac{1}{1+i\omega\tau} \tag{5}$$

If the dielectric system has a distribution of relaxation times, the right side of Eq. 5 should be duly amended.

The so-called "slopes" a' and a'' are defined in the usual way.[2] The dielectric constant ε' and loss ε'' of the dilute solutions are assumed to be represented by the empirical equations:

$$\left.\begin{aligned} &\varepsilon' = \varepsilon_1' + a'c_2 \\ &\varepsilon_0 = \varepsilon_{10} + a_0c_2, \quad \varepsilon_\infty = \varepsilon_{1\infty} + a_\infty c_2 \\ &\varepsilon'' = a''c_2 \end{aligned}\right\} \tag{6}$$

in which subscript 1 refers to the pure solvent and 2 to the solute while subscript 0 refers to the zero frequency measurement in the static field and ∞ to the infinite frequency measurement (at a very high frequency). The concentration of the solute c_2 has been usually expressed in the units of mole fraction[2] but it will be seen later that any concentration units can be used instead.

From Eqs. 6 and Eqs. 4 the following relations are obtained since the square terms such as $(a'c_2)^2$, $(a''c_2)^2$ are negligible for dilute solutions.

$$\left.\begin{aligned} p' &= p_1' + b'c_2 \\ p'' &= b''c_2 \end{aligned}\right\} \tag{7}$$

and

$$\left.\begin{aligned} b' &\simeq \frac{3a'}{(\varepsilon_1'+2)^2\left[1+\dfrac{2a'c_2}{\varepsilon_1'+2}\right]} \\ &\simeq \frac{3a'}{(\varepsilon_1'+2)^2} \\ b'' &\simeq \frac{3a''}{(\varepsilon_1'+2)^2\left[1+\dfrac{2a'c_2}{\varepsilon_1'+2}\right]} \\ &\simeq \frac{3a''}{(\varepsilon_1'+2)^2} \end{aligned}\right\} \tag{8}$$

Consequently, there exists a simple relation:

$$\frac{b''}{a''} \simeq \frac{b'}{a'} \tag{9}$$

If we write for $p(0)$ and $p(\infty)$ which are both real

$$\left.\begin{aligned} p(0) &= p_1(0) + b_0c_2 \\ p(\infty) &= p_1(\infty) + b_\infty c_2 \end{aligned}\right\} \tag{10}$$

we obtain

$$b_0 \simeq \frac{3a_0}{(\varepsilon'_{10}+2)^2}, \quad b_\infty \simeq \frac{3a_\infty}{(\varepsilon'_{1\infty}+2)^2}$$

Since

$$\varepsilon_1' \simeq \varepsilon_{10} \simeq \varepsilon_{1\infty} \tag{11}$$

$$\frac{b_0}{a_0} \simeq \frac{b_\infty}{a_\infty} \simeq \frac{b'}{a'} \tag{12}$$

Relations 9 and 12 are important and will be discussed later. Introducing Eqs. 7 and 10 into Eq. 5, the left side of Eq. 5 becomes

$$\frac{(p'-ip'')-p(\infty)}{p(0)-p(\infty)} = \frac{p'_1-p_1(\infty)+c_2(b'-b_\infty-ib'')}{p_1(0)-p_1(\infty)+c_2(b_0-b_\infty)} \tag{13}$$

For non-polar solvents which have no dielectric loss, there is an approximate relation

$$p_1' \simeq p_1(0) \simeq p_1(\infty) \tag{14}$$

which arises from Eq. 11. Both Eqs. 11 and 14 are not rigorously valid for any non-polar solvent; but observed deviations are usually very small to be ignored.

By the use of Eqs. 9 and 12

$$\frac{b'-b_\infty-ib''}{b_0-b_\infty} = \frac{a'-a_\infty-ia''}{a_0-a_\infty} \tag{15}$$

From Eqs. 5, 13, 14 and 15 one obtains for the system of a single relaxation time

$$\frac{a'-a_\infty-ia''}{a_0-a_\infty} = \frac{1}{1+i\omega\tau} \tag{16}$$

Equation 16 becomes

$$\frac{a^*-a_\infty}{a_0-a_\infty} = \frac{1}{1+i\omega\tau} \tag{17}$$

in which a complex slope a^* introduced.

$$a^* = a' - ia'' \tag{18}$$

The usual Debye equation for the polar liquid is

$$\frac{\varepsilon^*-\varepsilon_\infty}{\varepsilon_0-\varepsilon_\infty} = \frac{1}{1+i\omega\tau_M} \tag{19}$$

where the complex dielectric constant ε^*, the static dielectric constant ε_0 and the high frequency dielectric constant ε_∞ are used in places of a^*, a_0 and a_∞ in Eq. 17.

The macroscopic relaxation time τ_M differs from τ defined by Eq. 2;[7]

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[7] C. J. F. Böttcher, Ref. 1, p. 357, Eq. (10.51)

$$\tau_M = \tau \frac{\varepsilon_0+2}{\varepsilon_\infty+2} \tag{20}$$

However, τ_M becomes identical with τ for dilute solutions in a non-polar solvent (cf. Eq. 11).

Debye Equations

From the real part of Eq. 16 we obtain

$$\frac{a'-a_\infty}{a_0-a_\infty} = \frac{1}{1+\omega^2\tau^2} \tag{21}$$

From the imaginary part

$$\frac{a''}{a_0-a_\infty} = \frac{\omega\tau}{1+\omega^2\tau^2} \tag{22}$$

Equations 21 and 22 provide two independent values of the relaxation times for a solute molecule from the measured values of a' and a'' at a single frequency in the dispersion range.

Combination of these equations will lead to a set of two equations which are independent to each other.

$$a' = a_\infty + \frac{1}{\tau}\left(\frac{a''}{\omega}\right) \tag{23}$$

and

$$a' = a_0 - \tau(\omega a'') \tag{24}$$

The latter equations are useful in checking the validity of the Debye equations of a single relaxation time.

If the Debye equation of a single relaxation time is valid for the system under consideration and if the measurement is conducted with sufficient accuracy, we would be able to determine the relaxation time by use of any equation above mentioned. Accuracy of such a procedure was carefully examined for a few examples by Higasi and Kiyohara.[8)]

The equation derived originally by Debye for the same purpose is

$$\tan\vartheta = \frac{\varepsilon''}{\varepsilon'} \simeq \frac{(\varepsilon_1'+2)^2}{\varepsilon_1'}\,\frac{4\pi\mu^2c_2}{2700\boldsymbol{k}T}\boldsymbol{N}\frac{\omega\tau}{1+\omega^2\tau^2} \tag{25}$$

in which c the molar concentration and $\boldsymbol{N}$ is the Avogadro number. Equation 25 is a modified form of Eq. 22. Since there is a relation[9)] between the dipole moment μ and the two slopes a_0 and a_∞

$$\mu^2 \simeq B^2(a_0-a_\infty) \tag{26}$$

where

$$B^2 = \frac{1}{(\varepsilon_1'+2)^2}\,\frac{2700\boldsymbol{k}T}{4\pi\boldsymbol{N}} \tag{27}$$

Assuming $\varepsilon''=a''c_2$, $\varepsilon'=\varepsilon_1'$ for dilute solution Eq. 25 is shown to be identical with Eq. 22.

Gopola Krishna[5)] proposed a new method of determining the relaxation time from microwave measurement at a single frequency. His equation is:

$$x = P + \frac{1}{\omega\tau}y \tag{28}$$

in which

$$x = p',\quad y = p'' \text{ and } P = p(\infty) \tag{29}$$

Cf. Eqs. 3 and 4. τ is calculated from the slope of the graph, x against y.

For dilute solutions of a non-polar solvent we have the following equations (cf. Eqs. 7 and 10).

$$p' = p_1' + b'c_2,\quad p'' = b''c_2$$

and

$$p(\infty) = p_1(\infty) + b_\infty c_2$$

Hence Eq. 28 can be rewritten

$$\frac{1}{\omega\tau} = \frac{x-P}{y} = \frac{p_1'-p_1(\infty)+(b'-b_\infty)c_2}{b''c_2}$$

And from Eqs. 9, 12 and 14

$$\frac{1}{\omega\tau} = \frac{a'-a_\infty}{a''} \tag{30}$$

Eq. 30 is identical with Eq. 23.

Concluding Remarks

1) In obtaining slopes a' and a'' as defined

$$\left.\begin{aligned}\varepsilon' &= \varepsilon_1' + a'c_2\\ \varepsilon'' &= a''c_2\end{aligned}\right\} \tag{6}$$

there is no restriction on the choice of the concentration unit for the solute since the linear relationship is little affected by such a choice.[10)] Gram fraction, volume fraction or mole/litre can be used in place of the mole fraction usually employed. This will be evident at the inspection of Eq. 15 where all the c_2s are cancelled.

2) If a_0 is measured and a_∞ is estimated with reasonable accuracy, the relaxation time τ will be calculated either from the a' value or from a'' value measured at a single frequency in the dispersion range.

$$\tau = \frac{1}{\omega}\sqrt{\frac{a_0-a'}{a'-a_\infty}} \tag{31}$$

$$\tau = \frac{1}{\omega}[A \pm \sqrt{A^2-1}] \tag{32}$$

where

$$A = \frac{a_0-a_\infty}{2a''} \tag{33}$$

[8)] K. Higasi and O. Kiyohara, *Bull. Inst. Appl. Elec.*, **18**, 24 (1966).

[9)] K. Higasi, ibid., **4**, 231 (1952); *Bull. Inst. Phys. Chem. Research*, **22**, 865 (1943).

[10)] K. Higasi and K. Uchiyama, *Bull. Inst. Appl. Elec.*, **17**, 164 (1965).

If both a' and a'' are measured at a single frequency, τ will be calculated together with a_0 or a_∞.

$$\tau = \frac{1}{\omega}\frac{a_0 - a'}{a''} \tag{34}$$

$$\tau = \frac{1}{\omega}\frac{a''}{a' - a_\infty} \tag{35}$$

These equations are applicable only to the dilute solution system with a single relaxation time.

3) The ε', ε'' plot is based on the Cole-Cole equation:[11]

$$\frac{\varepsilon^* - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \frac{1}{1 + (i\omega\tau_0)^{1-\alpha}} \tag{36}$$

where τ_0 is the most probable relaxation time and α is the Cole-Cole parameter for representing the distribution of the relaxation times. Similarly the a', a'' plot is based on the following equation;

$$\frac{a^* - a_\infty}{a_0 - a_\infty} = \frac{1}{1 + (i\omega\tau_0)^{1-\alpha}} \tag{37}$$

Equation 37 will be obtained from Eq. 5, if the right side of Eq. 5 is assumed to be equal to $1/[1+(i\omega\tau_0)^{1-\alpha}]$.

From a measurement of a' and a'' at a single frequency in the dispersion region, one is able to find τ_0 and α by the following equations[12] which are derived from Eq. 37.

$$\tau_0 = \frac{1}{\omega}\left(\frac{A^2 + B^2}{C^2}\right)^{\frac{1}{2(1-\alpha)}} \tag{38}$$

$$1 - \alpha = \frac{2}{\pi}\tan^{-1}\frac{A}{B} \tag{39}$$

where

$$\left.\begin{aligned} A &= a''(a_0 - a_\infty) \\ B &= (a_0 - a')(a' - a_\infty) - a''^2 \\ C &= (a' - a_\infty)^2 + a''^2 \end{aligned}\right\} \tag{40}$$

Equations 38 and 39 for the Cole-Cole distribution are to be used only when all the values, a', a'', a_0 and a_∞ are obtained with high accuracy.

4) Compare the polarizability plot of $p' = p_1' + b'c_2$ vs. $p'' = b''c_2$ with the Cole-Cole plot of $\varepsilon' = \varepsilon_1' + a'c_2$ vs. $\varepsilon'' = a''c_2$. One will find that two semi-circles for dilute solutions should have the same shape, because there are proportionality relations between b''/a'', b'/a', etc. See Eqs. 9 and 12. Consequently the a', a'' plot becomes equivalent to the p', p'' plot[6] in this case.

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[11] K. S. Cole and R. H. Cole, *J. Chem. Phys.*, **9**, 341 (1941).

[12] See also G. L. Clark, ibid., **25**, 125 (1956).