

calc. No other choice of s and x is as satisfactory as this one. Thus from kinetic data alone s , x , and m are fixed; P can be calculated directly from these parameters; and b can be calculated from k_0' .

$$P \approx \frac{(m+s-1)! (1-e^{-x})^s e^{-mx}}{m!(s-1)! \left(1 - \frac{m+s}{m+1} e^{-x}\right)} = 0.98 \times 10^{-12}. \quad (33)$$

From the observed value of $k_0' = bP$, one finds b is 1.5×10^{13} cc mole⁻¹ sec⁻¹. With this value and Eq. (22) one gets 1.9×10^{-8} cm for the collisional diameter of nitrous oxide (the value from gas viscosity is 3.3×10^{-8}

cm). The frequency deduced from **F** and **G** is 730 cm⁻¹ (the fundamental frequencies of the normal modes are 1289, 588, 588, 2238 cm⁻¹). With all parameters of Kassel's theory determined, the theory predicts the form of k vs $[M]$ curve at all intermediate concentrations of M . The values of k at intermediate concentrations were calculated and compared with observed⁷ values at intermediate pressures. Unfortunately, the agreement at intermediate pressures was very poor. Thus there remains a conflict between Kassel's theory and these data at the intermediate pressures. At the present time it is not clear whether this conflict is due to poor data or to the theory.

Dielectric Dispersion in Materials Having a Distribution of Relaxation Times

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On the basis of considerable experimental evidence, a particular form for the dielectric loss factor, ϵ'' , is assumed to hold for many materials exhibiting a distribution of relaxation times. The dielectric constant, ϵ' , corresponding to the assumed form of ϵ'' is then computed by means of the Kronig-Kramers relations and tabulated as a function of log frequency and of the distribution function half-width parameter, α . Using these results, experimental ϵ' and ϵ'' curves can be easily tested for mutual consistency and can be fitted individually. In conclusion, a brief discussion of other methods of dealing with the many-relaxation-time dispersion problem is given.

INTRODUCTION

THIS paper is concerned with an extension of a much-used treatment of Fuoss and Kirkwood¹ of dielectric dispersion in materials exhibiting a distribution of relaxation times. For such materials, the simple Debye equations based on a single relaxation time do not correctly describe experimental results for the frequency dependence of the real dielectric constant, ϵ' , and the dielectric loss factor, ϵ'' , where the complex dielectric constant is given by $\epsilon^* = \epsilon' - i\epsilon''$. Instead, experimental curves are broader than Debye curves and can often be analyzed in terms of a parameter α ($0 \leq \alpha \leq 1$) which determines the half-width of the relaxation-time distribution function. When $\alpha = 1$, there is only a single relaxation time, while the distribution function and the dispersion curves become broader and broader as α decreases.

Fuoss and Kirkwood give a sensitive test for the applicability of their method to experimental dispersion data, and, when it is applicable, precise values can be obtained for α and for f_m , the frequency at which ϵ'' reaches its maximum value, ϵ_m'' . These two quantities, together with the scale factor, ϵ_m'' , obtained directly from measurement, are then sufficient to determine the

ϵ' and ϵ'' curves as functions of frequency within the dispersion region. Therefore, the variation of these derived quantities with temperature, impurity content, etc., is of considerable usefulness in interpreting dielectric data.

One of the main purposes of the paper of Fuoss and Kirkwood was to derive a general expression connecting the imaginary part of the reduced polarization, accounting for losses in the material, with the corresponding relaxation-time distribution function. In addition, they were also concerned with relating the reduced polarization to the complex dielectric constant and with obtaining the real part of the dielectric constant corresponding to a given specific form for the imaginary part which had been found to fit considerable experimental data. The Fuoss-Kirkwood treatment of these latter subjects is somewhat limited, however, by the use of the not-always applicable modified² Onsager³ relation between dielectric constant and polarization. The use of this relation leads them to useful results for the functional dependence of ϵ' and ϵ'' on frequency applicable only when $|\epsilon^*| \gg 1$ and $\epsilon'' \gg \epsilon'^2$. Finally, they only compute analytic forms of ϵ' for two specific fractional values of α , whereas for complete comparison

¹ R. M. Fuoss and J. G. Kirkwood, *J. Am. Chem. Soc.* **63**, 385 (1941).

² J. G. Kirkwood, *J. Chem. Phys.* **7**, 911 (1939).

³ L. Onsager, *J. Am. Chem. Soc.* **58**, 1486 (1936).

with experiment it would be useful to be able to determine the dependence of ϵ' on frequency for any α -value in the range from zero to unity.

In the present work, the starting point of the Fuoss-Kirkwood treatment is retained, but it is found unnecessary to introduce the Onsager formula and the results obtained hold without restriction. In addition, a family of curves and a table are presented through whose use ϵ' curves for comparison with experiment may be obtained for any α -value in the above range.

THE FORM OF THE DIELECTRIC LOSS FACTOR

One of the principal results of the Fuoss-Kirkwood paper is that the half-width parameter α may be determined from the slope of the function $\cosh^{-1}[\{\epsilon_m''(2+1/\epsilon_m''^2)\}/\{\epsilon''(2+1/\epsilon''^2)\}]$ plotted against the natural logarithm of the frequency, provided that such a test plot yields a straight line. Here ϵ_m' is the value of ϵ' at $f=f_m$. In data considered so far, ϵ_m' has always been fairly large compared to unity, and therefore the simpler function $\cosh^{-1}(\epsilon_m''/\epsilon'')$ could be used in place of the above form and a straight line still obtained. When this approximation is valid, Fuoss and Kirkwood found the empirical result $\epsilon'' = \epsilon_m'' \operatorname{sech} \alpha x$, where $x = \ln(f_m/f)$. This is the form which will be used in the present analysis. It must be emphasized that this expression for ϵ'' is thus obtained heuristically as that which best fits a large amount of dispersion data; it is not derived from a theoretical consideration of possible dispersion mechanisms.

When ϵ'' is well represented by such a function, $\cosh^{-1}(\epsilon_m''/\epsilon'') = \alpha x$. Therefore, α is given by the slope of the line $\cosh^{-1}(\epsilon_m''/\epsilon'')$ versus $\ln f$, and f_m is accurately determined from the intersection of this line with the $\cosh^{-1}(\epsilon_m''/\epsilon'') = 0$ axis.

DIELECTRIC CONSTANT FREQUENCY DEPENDENCE

Since the above simple expression for ϵ'' has been found to be capable of fitting a large amount of experimental ϵ'' dispersion data with $\alpha < 1$, it seemed worthwhile to attempt to obtain the corresponding expression for ϵ' as a function of α and x by using the Kronig-Kramers integrals.^{4,5} This approach differs considerably from that of Fuoss and Kirkwood, who assumed the $\operatorname{sech} \alpha x$ form for the imaginary part of the reduced polarization and by means of the Onsager relation and contour integration involving the relaxation-time distribution function itself arrived at approximate expressions for the dependence of ϵ' and ϵ'' on α and x .

The Kronig-Kramers integral relations connecting ϵ' and ϵ'' may be written in the form

$$\begin{aligned} \epsilon'(f) - \epsilon_\infty' &= \frac{2}{\pi} \int_0^\infty \epsilon''(\mu) \frac{\mu}{\mu^2 - f^2} d\mu, \\ \epsilon''(f) &= \frac{-2f}{\pi} \int_0^\infty \frac{[\epsilon'(\mu) - \epsilon_\infty'] d\mu}{\mu^2 - f^2}, \end{aligned} \tag{1}$$

where both integrals are principal values and ϵ_∞' is the value of ϵ' at very high (optical) frequencies. The above integrals are here assumed to cover two separate dispersion regions: that at medium or low frequencies which is postulated to involve a distribution of relaxation times, and that at infrared frequencies which occurs when the dipoles or ions of the material can no longer follow the applied alternating field.

We are particularly concerned with the former dispersion region and wish to use the first of the above integrals to obtain the analytical dependence of ϵ' on α and x when $\epsilon''(x)$ is given by $\epsilon_m'' \operatorname{sech} \alpha x$, $x = \ln(f_m/f)$, and f_m is a much lower frequency than that at which the final dispersion region occurs. Since the two dispersion regions are assumed to be widely separated, their contributions to ϵ' are essentially independent, and we may write

$$\epsilon'(f) - \epsilon_1' = \frac{2\epsilon_m''}{\pi} \int_0^\infty \frac{\mu \operatorname{sech}(\alpha \ln f_m/\mu) d\mu}{\mu^2 - f^2}, \tag{2}$$

where ϵ_1' is the dielectric constant for frequencies much higher than f_m (beyond the first dispersion region) yet much lower than the frequency of the infrared or very high frequency dispersion region. If only one dispersion region is present, ϵ_1' is identical with ϵ_∞' . The upper limit of integration in Eq. (2) can justifiably be extended to infinity because of the excellent exponential convergence produced by the hyperbolic term, which ensures that there will be negligible contribution from this integral for frequencies near the final dispersion region.

The integral (2) may be reduced to manageable form by the substitutions $\mu = f_m e^{\nu/\alpha}$ and $x = \ln f_m/f$. One then obtains

$$\epsilon'(x) - \epsilon_1' = \frac{2\epsilon_m''}{\pi\alpha} \int_{-\infty}^\infty \frac{d\nu}{\cosh \nu (1 - e^{-2x-2\nu/\alpha})}. \tag{3}$$

For future convenience, let us define the function $J(\alpha, x)$ by

$$\begin{aligned} J(\alpha, x) &= \frac{\alpha}{2\epsilon_m''} [\epsilon'(x) - \epsilon_1'] \\ &= \frac{1}{\pi} \int_{-\infty}^\infty \frac{d\nu}{\cosh \nu (1 - e^{-2x-2\nu/\alpha})}. \end{aligned} \tag{4}$$

It has been found that this integral may be evaluated by contour integration for any α -value of the form $(2n+1)/m$ where m and n are positive integers and $m > 0$. Zeros of $\cosh z$ occur for $z = \pm i\pi(l + \frac{1}{2})$, while zeros of $(1 - e^{-2x-2z/\alpha})$ occur when $z = \alpha(-x \pm i\pi k)$, and $l, k = 0, 1, 2 \dots$. The contour employed for the integration is rectangular and is defined by the points $z = \pm A$ and $z = \pm A + i\pi(2n+1)$. There is no contribution to the integral from the short sides of the rectangle at $z = \pm A$ when A approaches infinity. In order to carry out the integration, it is necessary that the integrand

⁴ R. Kronig, J. Opt. Soc. Am. 12, 547 (1926).

⁵ H. Kramers, Atti Congz. dei Fisici, Como, 545 (1927).

along the real axis be the negative of that along the $y = \pi(2n+1)$ axis. This will only be the case provided that $(2n+1) = m\alpha$; this equation determines those values of α for which the integral can be evaluated.

The contour is drawn so as to include within it the pole on the real axis at $z = -\alpha x (k=0)$ and to exclude the corresponding pole at $z = -\alpha x + i\pi(2n+1) (k=m$

$= (2n+1)/\alpha)$. It can be shown, however, that the residue of the pole on the real axis at $z = -\alpha x$ contributes nothing to the principal value of the integral. Thus, the residues at the following poles inside the contour must be evaluated: $z = i\pi(l + \frac{1}{2}), 0 \leq l \leq 2n$; $z = \alpha(-x + i\pi k), 1 \leq k \leq m-1$. The residues are found to be

$$R_l = \frac{-\left[e^{-2x} \frac{\pi}{\alpha} \sin \pi(2l+1) + i \left\{ 1 - e^{-2x} \cos \pi(2l+1) \right\} \right]}{\pi \sin \pi(l + \frac{1}{2}) \left[\left\{ e^{-2x} \frac{\pi}{\alpha} \sin \pi(2l+1) \right\}^2 + \left\{ 1 - e^{-2x} \cos \pi(2l+1) \right\}^2 \right]}, \tag{5}$$

$$R_k = \frac{\alpha \cos \alpha k \pi \cosh \alpha x + i \sin \alpha k \pi \sinh \alpha x}{2\pi (\cos \alpha k \pi \cosh \alpha x)^2 + (\sin \alpha k \pi \sinh \alpha x)^2}$$

The function $J(\alpha, x)$ can easily be shown to equal $i\pi(\sum_l R_l + \sum_k R_k)$ where the values of l and k are as above. The real part of the sum of the residues is identically zero.

On evaluating $J(\alpha, x)$ for several values of α , it was found to be identical with a similar function used by Fuoss and Kirkwood and defined by them in terms of another equivalent but more complicated definite integral. It appears that the equivalence of the two definite integral expressions for $J(\alpha, x)$, both involving ϵ'' in their integrands, may impose an interesting restriction on the analytic forms of ϵ'' suitable for representing the loss factor of a many-relaxation-time material and yet consistent, together with its pair ϵ' , with the Kronig-Kramers relations. In Fuoss and Kirkwood's analysis, $J(\alpha, x)$ is the real part of the reduced polarization, Q , and is related to ϵ' by means of the modified Onsager relation. The result there obtained is

$$J(\alpha, x) \cong \frac{\alpha}{4\epsilon_m''} \left[2\epsilon'(x) - 1 - 1/\epsilon'(x) - \frac{(n^2-1)(2n^2+1)}{n^2} \right], \tag{6}$$

where $n^2 = \epsilon_\infty'$ and is the square of the index of refraction of the material. For comparison, the present treatment gives

$$J(\alpha, x) = \frac{\alpha}{2\epsilon_m''} [\epsilon'(x) - \epsilon_1']. \tag{7}$$

Since $J(\alpha, \infty) = 1$, we may also write

$$\epsilon'(x) - \epsilon_1' = (\epsilon_0' - \epsilon_1') J(\alpha, x), \tag{8}$$

where ϵ_0' is the static dielectric constant.

The fact that the real part of the reduced polarization of Fuoss and Kirkwood is found to be directly related

to the real part of the dielectric constant for the specific case of the hyperbolic form for ϵ'' is not surprising. In fact, it can be shown⁶ that the following relation connects the complex dielectric constant, ϵ^* , and the reduced polarization, Q , of Fuoss and Kirkwood

$$\epsilon^* - \epsilon_1' = (\epsilon_0' - \epsilon_1') Q,$$

provided only that the principle of superposition applies (implying the independence of different relaxation mechanisms).

Because of the complexity of their integral for $J(\alpha, x)$, Fuoss and Kirkwood evaluated it explicitly only for $\alpha = \frac{1}{3}$ and $\alpha = \frac{1}{2}$. If, in addition, the results of the present work are used, the following expressions for $J(\alpha, x)$ may be given:

$$J(1, x) = (1 + e^{-2x})^{-1}, \tag{9}$$

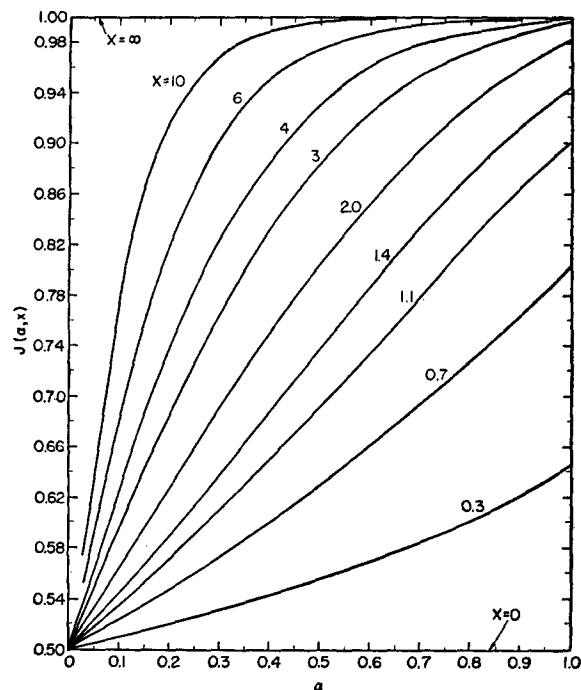
$$J(\frac{3}{2}, x) = \frac{3}{8 \sinh(3x/4)} \frac{1}{1 - e^{-2x}} + \frac{2(1 + \frac{1}{2}e^{-2x})}{(1 + \frac{1}{2}e^{-2x}) + \frac{3}{4}e^{-4x}} \frac{3\sqrt{2} \sinh(3x/4)}{4 \cosh(3x/2)}, \tag{10}$$

$$J(\frac{1}{2}, x) = (1 - e^{-2x})^{-1} - (4 \sinh(x/2))^{-1}, \tag{11}$$

$$J(\frac{1}{3}, x) = \frac{1}{1 + e^{-2x}} \frac{2 \sinh(x/3)}{\sqrt{3}(2 \cosh(2x/3) - 1)}, \tag{12}$$

$$J(\frac{1}{5}, x) = \frac{1}{1 + e^{-2x}} \frac{\sinh(x/5)}{5} \times \sum_{j=1}^2 \frac{\sin(j\pi/5)}{\cosh^2(x/5) - \sin^2(j\pi/5)}, \tag{13}$$

⁶ H. Fröhlich, *Theory of Dielectrics* (Clarendon Press, Oxford, England, 1949), p. 91.

FIG. 1. The function $J(\alpha, x)$.

$$J\left(\frac{1}{10}, x\right) = \frac{1}{1 - e^{-2x}} - \frac{1}{20 \sinh(x/10)} - \frac{\sinh(x/10)}{10} \sum_{j=1}^4 \frac{\sin(j\pi/10)}{\cosh^2(x/10) - \sin^2(j\pi/10)}, \quad (14)$$

$$J(0, x) = \frac{1}{2} \quad J(\alpha, 0) = \frac{1}{2}, \quad (15)$$

$$J(\alpha, x) + J(\alpha, -x) = 1. \quad (16)$$

Expressions for $J(\alpha, x)$ for other fractional α -values may easily be calculated from the residues given in Eqs. (5). The above formulas for $J(\alpha, x)$ are sufficient, however, for the computation of the family of parametric curves presented in Fig. 1. Using curves of this nature, the values of $J(\alpha, x)$ as a function of x may be read off directly for any experimental values of α . Thus, when α has been determined from the straight-line plot of $\cosh^{-1}(\epsilon_m''/\epsilon'')$ versus $\ln f$, Fig. 1 and Eq. (7) may be used to compute $\epsilon'(x) - \epsilon_1'$. If ϵ_1' is determined experimentally or is independently known, $\epsilon'(x)$ derived in the above fashion may then be compared directly with the experimental $\epsilon'(x)$ curve. For greater accuracy, the data used in plotting the curves of Fig. 1 are presented in Table I, so that the curves may be replotted on graph paper.

An example of curve fitting using the above method is presented in Fig. 2 for dispersion data obtained by Fuoss⁷ on polyvinyl chloride-diphenyl. The \cosh^{-1} plot yielded a good straight line from which the values of α and f_m shown on the figure were obtained. Then the

⁷ R. M. Fuoss, J. Am. Chem. Soc. **63**, 378 (1941).

$\epsilon'(x) - \epsilon_1'$ curve was computed with the aid of Fig. 1 and the applicable α -value. Since ϵ_1' was not measured by Fuoss, it was necessary to select a value of this constant which gave best agreement with the experimental ϵ' points. The calculated curves are symmetric and antisymmetric about $x=0$, and it will be seen that although this is the case for the experimental ϵ'' points, there is a progressive deviation of the experimental ϵ' points from the calculated curve at high frequencies. This deviation is a real effect and is discussed to some extent by Fuoss.⁷ It indicates either that the hyperbolic form for ϵ'' is not a sufficiently good approximation for this material or that there is another dispersion region sufficiently near that considered here that the separation procedure used in this paper is not completely valid. The latter is probably the correct explanation since ϵ_∞' is known not to exceed 2.5 for this material whereas the best value of ϵ_1' is found to be 2.9.

CONCLUSION

In conclusion, it is worth while to discuss briefly the relation of this method of treating many-relaxation-time data with others which have been developed. The first such method is due to Maxwell⁸ and Wagner⁹ and assumes that the relaxation times are distributed according to a normal law around a most probable relaxation time. Comparison of the results of this assumption with experimental data is difficult, although such comparison has been somewhat simplified by a graphical method developed by Yager.¹⁰ In the remaining methods to be considered, the forms of the distribution function are determined essentially from the experimental data. Rather than assuming *ab initio* the form of the relaxation-time distribution function, in these latter methods, an assumed, relatively general, form for the experimental dispersion data (such as the present hyperbolic form for ϵ'') is used from which to derive the applicable distribution function. The latter is the preferable approach since it makes more direct use of the results of dispersion measurements.

TABLE I. Calculated values of the function $J(\alpha, x)$.

$\alpha \backslash x$	1	3/4	1/2	1/3	1/5	1/10	0
0	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
0.30	0.646	0.593	0.558	0.535	0.520	0.511	$\frac{1}{2}$
0.70	0.803	0.711	0.629	0.581	0.547	0.523	$\frac{1}{2}$
1.1	0.900	0.801	0.691	0.623	0.571	0.532	$\frac{1}{2}$
1.4	0.943	0.856	0.736	0.655	0.588	0.540	$\frac{1}{2}$
2.0	0.982	0.914	0.806	0.710	0.628	0.562	$\frac{1}{2}$
3.0	0.998	0.965	0.885	0.789	0.686	0.595	$\frac{1}{2}$
4.0	1	0.984	0.931	0.847	0.736	0.625	$\frac{1}{2}$
6.0	1	0.996	0.975	0.923	0.819	0.682	$\frac{1}{2}$
10	1	1	0.997	0.979	0.917	0.777	$\frac{1}{2}$
∞	1	1	1	1	1	1	—

⁸ J. C. Maxwell, *Electricity and Magnetism* (Oxford University Press, London, England, 1889), Vol. 1.

⁹ K. W. Wagner, Ann. Physik **40**, 817 (1913).

¹⁰ W. A. Yager, Physics **7**, 434 (1936).

Cole and Cole¹¹ observed that when experimental values of ϵ' and ϵ'' are plotted *versus* one another on the complex plane, a good circular arc whose center lies on or below the ϵ' axis is often obtained. When this is the case, it is then possible to compute the analytic dependence of ϵ' and ϵ'' on frequency required by such a curve. Further, the intersections of the circular arc with the ϵ' -axis give ϵ_0' and ϵ_∞' (or ϵ_1' if the measured dispersion region is not the one of highest frequency). From the displacement of the circle center below the ϵ' -axis, the distribution function half-width parameter may be obtained. The expressions derived for ϵ' , ϵ'' , and the corresponding distribution function are quite similar to those arising from the Fuoss-Kirkwood treatment. This approach of Cole and Cole has the advantage of supplying an easy test for the applicability of their method and for the mutual consistency of ϵ' and ϵ'' data. However, it is not as easy to compare the precise agreement of experimental ϵ' and ϵ'' values individually with the corresponding analytic forms for these quantities as it is using the Fuoss-Kirkwood approach together with the results of the present work.

When the algebraic forms given herein for ϵ' and ϵ'' as functions of frequency are plotted on the complex ϵ' , ϵ'' plane according to the method of Cole and Cole, a good circular arc is obtained for values of α near unity. As α decreases, however, it is found that if a circular arc is drawn through the $(\epsilon_m', \epsilon_m'')$ and $(\epsilon_0', 0)$, $(\epsilon_1', 0)$ points, intermediate points fall progressively farther inside the arc and the calculated points tend to approach the ϵ' -axis along straight lines rather than along the arc. Here ϵ_m' is the value of ϵ' for the frequency at which ϵ'' is a maximum and is equal to $\epsilon_1' + \epsilon_m''/\alpha = \epsilon_1' + (\epsilon_0' - \epsilon_1')/2$. Although the Cole-Cole formulas give this same value for ϵ_m' , they lead to an expression for ϵ_m'' different from that following from the present treatment. Because they both lead to the Debye equations for $\alpha=1$, it is difficult to determine whether the Cole-Cole or the Fuoss-Kirkwood assumption most nearly describes the experimental results for α -values near unity, but distinction becomes progressively more certain as α decreases.

Recently, Davidson and Cole¹² have proposed a new analytic form for ϵ^* applying to many-relaxation-time materials. This formula yields a circular arc when plotted on the ϵ' , ϵ'' plane, except that the approach to the ϵ' -axis at high frequencies may be along a straight line rather than along the arc. In the present treatment, the approach to the ϵ' -axis is along straight lines

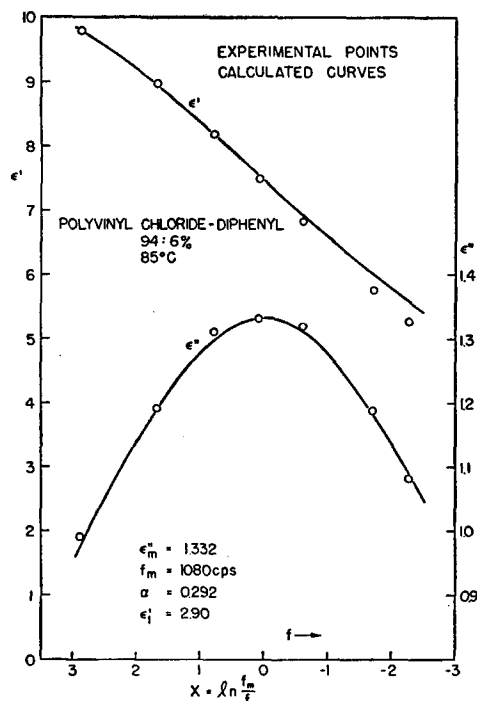


Fig. 2. Real and imaginary dielectric constants of polyvinyl chloride-diphenyl, 94:6, at 85°C (after Fuoss, reference 7).

(for small α) for both high and low frequencies. Considerable experimental data have been well fitted by Davidson and Cole, but their method does not seem to allow the data of Fuoss presented in Fig. 2 of this paper to be fitted as closely as does the present analysis.

It is not possible to say at this point that any one of the above approaches is more nearly correct, to the exclusion of the other methods, for all dispersion data involving a distribution of relaxation times. Considerable published data have been fitted with the use of either the Cole-Cole, the Fuoss-Kirkwood, or the Davidson-Cole methods, however, and it is likely that each has its own exclusive sphere of applicability. In specific cases, it may be important to determine which approach allows experimental data to be fitted most accurately in order to aid in the development of a detailed theory of the relaxation processes occurring in the material. Some possible mechanisms leading to deviations from the simple Debye dispersion curves are discussed by Cole and Cole.¹⁰

ACKNOWLEDGMENT

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

¹² D. W. Davidson and R. H. Cole, *J. Chem. Phys.* **19**, 1484 (1951).