or in other words, at the transition from brittle to elastic. Furthermore, if we put on the log E–T curves the temperature at which the loss factor for a given frequency reaches its peak, we find that the modulus at the temperature of maximum loss varies by about a factor of two for this range of composition. This is about what would be expected from Maxwell's equation[6]

$$\eta = (1/2)\left(\frac{1}{1+\mu}\right)E_0\lambda \qquad (12)$$

where η is viscosity, μ is Poisson's ratio, E_0 is the coefficient of Young's modulus in the form $E = E_0e^{-(t/\lambda)}$ and λ is the time of elastic relaxation. We previously showed (Table I) that the d. c. conductance was constant at the temperature of maximum absorption for a given frequency for different concentrations of diphenyl and argued that this means equal viscosities. Then if η is constant, we have $E_0\lambda$ constant, and since λ decreases with increasing temperature, the modulus should increase with increasing temperature, as is actually the case according to the data shown in Fig. 13. We hope to find further correlations between electrical and mechanical properties of these systems, which may lead to a clearer understanding of the molecular mechanism involved.

Summary

1. The system polyvinyl chloride–diphenyl has been studied over the ranges −70 to +100°, 60 cycles to 10 kilocycles and 0–20% diphenyl.

2. Further evidence that the electrical properties of polar polymers are due to a viscosity controlled relaxation mechanism is given.

3. As a function of composition, the loss factor for a given frequency and temperature goes through a maximum at a concentration which is characteristic of a given plasticizer.

4. The low temperature absorption in polar polymers is reduced and eventually eliminated by the addition of a second component.

5. The electrical properties are markedly non-linear in composition in the low concentration range of compositions.

SCHENECTADY, NEW YORK RECEIVED AUGUST 3, 1940

(6) Maxwell, *Phil. Mag. J. Sci.*, IV, **35**, 134 (1867).

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC CO.]

Electrical Properties of Solids. VIII. Dipole Moments in Polyvinyl Chloride–Diphenyl Systems*

BY RAYMOND M. FUOSS AND JOHN G. KIRKWOOD

I. Introduction.—It is now well known that the electrical properties of polar systems containing giant molecules differ markedly from those in which the dipoles are on small molecules. The properties of the latter are well accounted for by Debye's theory of anomalous dispersion in which the fundamental assumption is a finite time of relaxation, specified by the size and shape of the polar solute molecule and the temperature and viscosity of the solvent. Three characteristic differences between the polymeric systems and the systems describable in terms of a single relaxation time appear: (1) the inflection slopes of the dielectric constant log–frequency curves are much lower in the former; (2) the corresponding loss factor log–frequency curves have a much larger half-width; and (3) the maximum loss factor is always much less than half the difference between the static dielectric constant and the square of the index of refraction. These differences can all be accounted for by assuming that many times of relaxation rather than a single one are involved. Wagner[1] assumed a Gaussian distribution of relaxation times in order to account for discharge curves, and Yager[2] has developed a method for applying the Gauss distribution to an analysis of a. c. data. We have, however, no actual proof of the necessity for the existence of a distribution of relaxation times for a given system, nor have we any right to assume that a possible distribution should be Gaussian. In fact, for data on polyvinyl chloride systems[3] it has been shown that the Gauss distribution will not reproduce the experimental results.

It is, of course, qualitatively plausible that a system containing a polar polymer should exhibit a distribution of relaxation times, because every di-

* Presented at the Fifth Annual Symposium of the Division of Physical and Inorganic Chemistry of the American Chemical Society, Columbia University, New York, December 30, 1940 to January 1, 1941.

(1) Wagner, *Ann. Physik*, **40**, 817 (1913).

(2) Yager, *Physics*, **7**, 434 (1936).

(3) Fuoss, THIS JOURNAL, **63**, 369, 378 (1941).

pole in a given chain is coupled to neighboring dipoles of the same chain by primary valence bonds, so that the motion of any dipole affects the motion of its neighbors, and they in turn influence its response to a torque. Furthermore, in the various configurations which a chain molecule can assume[4,5] we can find now one, now another segment of the chain acting effectively as a coöperating electrical unit, and these segments will, of course, vary in length between the two improbable extremes of a single monomeric unit and the whole extended chain. In a later paper we shall show that a linear polymer *must* exhibit a distribution of relaxation times as a necessary consequence of its structure.

In this paper, we present a solution of the following problem: given the loss-factor log-frequency curve, to find the distribution function for the relaxation times. A unique solution is presented for the case where the data can be empirically represented by an integrable analytic function. For polar polymers of the type described so far in this series of papers, we find

$$\epsilon'' \approx A \operatorname{sech} \alpha x \qquad (1)$$

where ϵ'' is the loss factor, A is a constant characteristic of the system and derivable from dielectric constant data, α is a parameter which measures the width of the distribution and x is the natural logarithm of the ratio of the frequency at maximum absorption to the frequency at which ϵ'' is measured. (For a single relaxation time, α obviously is unity and Eq. 1 reduces to the Debye formula.) The approximate equality sign appears because a function $H(x)$ is actually used in place of ϵ'', which is, for the cases treated here, closely proportional to ϵ''. The function $H(x)$ was introduced in order to eliminate much of the needless awkward algebra usually encountered in separating a complex quantity (the a. c. vector) into its real and imaginary parts.

It is convenient to use a logarithmic scale for the relaxation times. Let τ_m be the relaxation time corresponding to maximum H and

$$s = \ln \tau/\tau_m \qquad (2)$$

Define

$$F(s) = \tau G(\tau) \qquad (3)$$

where $G(\tau)$ is the distribution function for the relaxation times. It will then be shown that

$$\pi F(s) = H(s + i\pi/2) + H(s - i\pi/2) \qquad (4)$$

is a general relationship connecting the distribution of relaxation times and the electrical properties.

These properties of a polar system are in last analysis an average over the dipoles present in the system, and we should therefore be able to derive the average moment $\bar{\mu}$ per monomer unit from measurements of volume properties of polar polymers. This calculation will be made for the case of a polymer of the alternating structure $(-CH_2{\cdot}CHX-)_n$, where X is a simple polar group. It is based on the modified[6] Onsager[7] field, which must be used to replace the Lorentz field in condensed systems. If free rotation at each bond is permitted (or else restricted rotation with three equally probable energy minima), the average moment is given by

$$\bar{\mu} = \sqrt{3}\mu_0/2 \qquad (5)$$

where μ_0 is the moment of the equivalent group isolated in free space. Comparison with experimental data for the system polyvinyl chloride–diphenyl verifies Eq. 5 and, furthermore, confirms the conclusion previously reached on empirical grounds that the dipole–dipole interaction usually described as association in polar liquids is negligible for the type of polar polymers considered here.

II. The Reduced Polarization.—In previous treatments of electrical properties of matter, the generalized dielectric constant

$$\epsilon = \epsilon' - i\epsilon'' \qquad (6)$$

introduced by Debye has usually been the basis of the calculation. Here ϵ' is the ordinary dielectric constant, and ϵ'' is the loss factor. Phenomenologically, however, we are concerned with the polarization P per unit volume. It is possible to set up a relationship between P and ϵ, but since they are both complex quantities, most calculations become needlessly complicated on account of the algebraic manipulations involved in separating their components. A quantity, $Q(\omega)$, the reduced polarization, will be introduced: as will be seen below, it is intermediate between P and ϵ, and either is very simply derivable from it. Mathematical analysis of data and subsequent theoretical treatment lose much of their previous trivial awkwardness, when calculations are based on the components of $Q(\omega)$.

For a two component system, with mole fractions x_1 and x_2 of components of molecular weight

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[4] Kuhn, *Kolloid-Z.*, **68**, 2 (1934).

[5] Guth and Mark, *Monatsh.*, **65**, 93 (1934).

[6] Kirkwood, *J. Chem. Phys.*, **7**, 911 (1939).

[7] Onsager, THIS JOURNAL, **58**, 1486 (1936).

M_1 and M_2, we have, by an obvious extension of the modified Onsager theory[8]

$$\frac{(\epsilon - 1)(2\epsilon + 1)}{9\epsilon}\,\frac{M_1x_1 + M_2x_2}{\rho} = P_1x_1 + P_2x_2 \quad (7)$$

If we assume that the first component is non-polar and the second has permanent dipoles, we may set

$$P_1 = 4\pi N\alpha_1/3 \quad (8)$$

and

$$P_2 = (4\pi N/3)[\alpha_2 + (\mu\cdot\bar{\mu})_{av}/3kT] \quad (9)$$

where α_1 and α_2 are the electronic polarizations and $(\mu\cdot\bar{\mu})_{av}$ is averaged over all internal configurations of the molecule. In (9), μ is the moment of a molecule of species 2 while $\bar{\mu}$ is the vector sum of μ and the moment induced by the molecule in its environment. Substituting (8) and (9) into (7), we find

$$\left\{\frac{(\epsilon - 1)(2\epsilon + 1)}{9\epsilon} - \frac{(n^2 - 1)(2n^2 + 1)}{9n^2}\right\} = P_2'x_2/V \quad (10)$$

where n is the index of refraction,

$$P_2' = 4\pi N\mu\cdot\bar{\mu}/9kT \quad (11)$$

and the molar volume V is given by

$$\rho V = M_1x_1 + M_2x_2 \quad (12)$$

For further simplification, let

$$\varphi(x) = (x - 1)(2x + 1)/x \quad (13)$$

Then (10) becomes

$$[\varphi(\epsilon) - \varphi(n^2)]V = 9P_2'x_2 \quad (14)$$

The above equations derived for a static field may be extended to the general a. c. case. We denote by $P_2'(\omega)$ the polarization at frequency $f = \omega/2\pi$ and define the reduced polarization as

$$Q(\omega) = \frac{P_2'(\omega)}{P_2'(0)} = \frac{\varphi(\epsilon) - \varphi(n^2)}{\varphi(\epsilon_0) - \varphi(n^2)} \quad (15)$$

where $P_2'(0)$ is the value of P_2' at zero frequency, corresponding to the static dielectric constant ϵ_0. For a given system, the quantity

$$Z = [\varphi(\epsilon_0) - \varphi(n^2)]/9 \quad (16)$$

is a normalizing constant independent of frequency. We can separate Q into its components as follows

$$Q(\omega) = J(x) - iH(x) \quad (17)$$

where

$$x = \ln \omega_m/\omega \quad (18)$$

with ω_m as 2 π times the frequency at maximum H. Separating $\varphi(\epsilon)$, using (6), we find

$$\varphi(\epsilon) = 2\epsilon' - 1 - \frac{\epsilon'}{\epsilon'^2 + \epsilon''^2} - i\epsilon''\left[2 + \frac{1}{\epsilon^{2'} + \epsilon''^2}\right] \quad (19)$$

For the cases to be considered in this paper

$$\epsilon'^2 >> \epsilon''^2 \quad (20)$$

so that to a rather close approximation

$$\varphi(\epsilon) = 2\epsilon' - 1 - 1/\epsilon' - i(2\epsilon'') \quad (21)^*$$

Comparing real and imaginary parts of (17) and (19), we find

$$J(x) = [2\epsilon' - 1 - 1/\epsilon' - \varphi(n^2)]/9Z \quad (22)^*$$

and

$$H(x) = 2\epsilon''/9Z \quad (23)^*$$

From the form of (22) and (23), we see that ϵ' and ϵ'' are easily determined if J and H are known, and conversely; provided, in both cases, that Z is known. $Q(\omega)$ in turn is very simply related to P'_2 by (15), and the latter to the moment by (11). It will also turn out that $Q(\omega)$ is a very convenient function to use when distributions of relaxations are involved.

III. Determination of the Distribution Function.—By an extension of the Debye theory of anomalous dispersion to a molecule with a large number of internal rotatory degrees of freedom, it can be demonstrated that

$$Q(\omega) = \int_0^\infty \frac{G(\tau)}{1 + i\omega\tau}\,\mathrm{d}\tau \quad (24)$$

where $G(\tau)$ is a distribution function in relaxation time, such that $G(\tau)\mathrm{d}\tau$ specifies the fraction of the total dipole moment of a molecule associated with relaxation times in the interval between τ and $\tau + \mathrm{d}\tau$. From its definition, it follows that $G(\tau)$ satisfies the following normalization condition

$$\int_0^\infty G(\tau)\mathrm{d}\tau = 1 \quad (25)$$

When $G(\tau)$ is a delta function $\delta(\tau - \tau_0)$, the result reduces to the familiar Debye theory for a single time of relaxation τ_0.

Separating (24) into its components, we find

$$J(x) = \int_{-\infty}^{\infty} F(s)\mathrm{d}s/[1 + e^{2(s-x)}] \quad (26)$$

and

$$H(x) = \int_{-\infty}^{\infty} e^{s-x}\,F(s)\mathrm{d}s/[1 + e^{2(s-x)}] \quad (27)$$

where by definition

$$s = \ln \tau/\tau_m \quad (28)$$

and

$$\tau G(\tau) = F(s) \quad (29)$$

If we define a kernel K by the equation

$$K(t) = e^t/(1 + e^{2t}) = (\operatorname{sech} t)/2 \quad (30)$$

(27) becomes

$$H(x) = \int_{-\infty}^{\infty} K(s - x)F(s)\,\mathrm{d}s \quad (31)$$

The physical problem stated in the introduction: "given the loss factor–frequency curve, to

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[8] Ref. 6, Eq. 13.

* Equations marked with an asterisk are subject to the approximation (20).

find the distribution of relaxation times" can now be restated as a mathematical problem. Given a function $H(x)$, to find a function $F(s)$ when the two are related by the integral equation (31) containing the kernel K. The integral equation can be solved by the use of Fourier transforms.[9]

The Fourier transform $L_H(u)$ of $H(x)$ is defined as

$$L_H(u) = \int_{-\infty}^{\infty} H(x)e^{iux}\,\mathrm{d}x \tag{32}$$

Substituting (31) for $H(x)$, we have

$$L_H(u) = \int_{-\infty}^{+\infty}\!\!\int K(s - x)\, F(s)\, e^{iux}\,\mathrm{d}x\,\mathrm{d}s \tag{33}$$

By introducing a new variable

$$t = s - x$$

and carrying out the integration over t holding s constant, (33) separates as follows

$$L_H(u) = \left(\int_{-\infty}^{\infty} K(t)\, e^{-iut}\,\mathrm{d}t\right)\left(\int_{-\infty}^{\infty} F(s)\, e^{ius}\,\mathrm{d}s\right)$$

which gives the result

$$L_H(u) = L_K(-u)\, L_F(u) \tag{34}$$

Then by the inversion theorem

$$F(s) = \frac{1}{2\pi}\int_{-\infty}^{\infty} [L_H(u)/L_K\,(-u)]\, e^{-ius}\,\mathrm{d}u \tag{35}$$

We next compute $L_K(-u)$. Consider the contour integral

$$I = \oint e^{iuz}\,\mathrm{sech}\, z\,\mathrm{d}z \tag{36}$$

around the rectangle bounded by the real axis, two verticals at $x = \pm A$ and a parallel to the real axis at $y = iB$. It can easily be shown that the integrals along all but the real axis vanish as A and B approach infinity. Hence (35) becomes

$$I = \int_{-\infty}^{\infty} \cos ux\,\mathrm{sech}\, x\,\mathrm{d}x \tag{37}$$

which is twice the Fourier transform of $K(t)$. The integrand in (36) has simple poles on the imaginary axis at the points

$$z_n = (n + 1/2)\pi i = y_n \tag{38}$$

and therefore by the Cauchy residue theorem

$$\begin{aligned} I &= 2\pi i \sum ie^{-y_n}/(-\sin y_n) \\ &= 2\pi \sum (-)^n\, e^{-u(n+1/2)\pi} \end{aligned} \tag{39}$$

Summing the geometric series in (39), we have finally

$$L_K(u) = (\pi/2)\,\mathrm{sech}\,(\pi u/2) = L_K(-\,u) \tag{40}$$

If now we substitute this result in (35), we obtain

$$F(s) = \frac{1}{\pi^2}\int_{-\infty}^{\infty} \cosh\,(u\pi/2)\, L_H\,(u)\, e^{-ius}\,\mathrm{d}u \tag{41}$$

Rewriting the transform of $H(x)$ as an integral, we find

$$F(s) = \frac{1}{\pi}\frac{1}{2\pi}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} H(x)\,[e^{-iu(s-x+i\pi/2)} + e^{-iu(s-x-i\pi/2)}]\,\mathrm{d}x\,\mathrm{d}u$$

But this is simply the Fourier transform of the inverse function and, by inspection, we see that

$$\pi F(s) = H(s + i\pi/2) + H(s - i\pi/2) \tag{42}$$

Our result now is that if we are given H as a function of x, *i. e.*, the experimental $\epsilon'' - \log f$ curve, and know f_m, and can represent $H(x)$ by an integrable analytic function, we can then compute directly from the experimental data the function $F(s)$ which gives the distribution of the times of relaxation by (29). (The conditions analytic and integrable are sufficient for the application of the Fourier inversion.) The function $G(\tau)$ so obtained will be as good an approximation of the real distribution as the empirical interpolation function $H(x)$ is for the data. On account of the exponential convergence of the functions naturally[10] involved in this general type of problem, the accuracy will be best if the data contain H_{max}, because then the large part of the integrals (26) and (27) near $x = 0$ are accurately determined, and the error in the empirical function for the exponential wings becomes a small part of the total integral.

IV. The Empirical Distribution Function.—Of a number of empirical interpolation formulas which might have been chosen to represent the data, the following was found to be the most satisfactory

$$H(x) = H(0)\,\mathrm{sech}\,\alpha x \tag{43}$$

Here $H(0)$ is, of course, the maximum value of $H(x)$, corresponding to $f = f_m$ and α is a parameter which determines the width of the H-curve at half-height. The form of (43) was suggested by the fact that for a single time of relaxation, where $G(\tau)$ is a Dirac delta function, the Debye theory gives $\epsilon''/\epsilon''_m = \mathrm{sech}\, x$.

If we substitute (43) in (42), we find

$$\frac{F(s)}{H(0)} = \frac{2}{\pi}\,\frac{\cos\,(\alpha\pi/2)\cosh\,\alpha s}{\cos^2\,(\alpha\pi/2) + \sinh^2\,\alpha s} \tag{44}$$

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[9] Titchmarsh, "Fourier Integrals and Transforms," Chap. XI, Oxford, 1937.

[10] "Naturally," because the term $(1 + i\omega\tau)$ in $\mu(\omega)$ leads to $(1 + \omega^2\tau^2)$ on separating into real and imaginary parts, and conversion to a log-scale of frequency thus automatically introduces a hyperbolic cosine in the denominator.

From the condition (25), which is equivalent to

$$\int_{-\infty}^{\infty} F(s)\,ds = 1 \qquad (45)$$

we obtain by use of (44)

$$H(0) = \alpha/2 \qquad (46)$$

But by (23), we then have the result

$$4\epsilon''_m/9Z = \alpha \qquad (47)$$

In order to determine α, we plot

$$\cosh^{-1}\,[H(0)/H(x)] = \cosh^{-1}\left\{\frac{\epsilon''_m(2 + 1/\epsilon'^2_m)}{\epsilon''\,(2 + 1/\epsilon'^2)}\right\} \qquad (48)^*$$

against the logarithm of the frequency; according to (43), α is determined by the slope of the resulting straight line (Fig. 1) and the intersection of the line with the horizontal axis determines f_m. Then with the experimental values of ϵ''_m and of α, we can calculate Z by (47). This in turn gives us a value of the static dielectric constant, according to (16), which finally may be used to compute the mean moment per molecule.

For comparison with experiment, several other useful relationships will next be derived. First, it is of interest to determine the half-width of the distribution function for the relaxation times. To find this, we determine s^* such that

$$F(s^*)/F(0) = 1/2 \qquad (49)$$

This is equivalent to solving the transcendental equation

$$2 = \cosh\zeta + \operatorname{sh}\zeta\ \operatorname{th}\zeta\ \operatorname{tn}^2 \alpha\pi/2 \qquad (50)$$

where

$$\zeta = \alpha\, s^* \qquad (51)$$

When ζ is small, (50) is equivalent to

$$\alpha = (2/\pi)\operatorname{tn}^{-1}(1/\zeta) \qquad (52)$$

and when α is small, to

$$2 = \cosh\zeta + \pi^2\alpha^2\zeta^2/4 \qquad (53)$$

Otherwise, successive approximations must be used. A number of solutions of (50) are given in Table I.

TABLE I

SOLUTIONS OF EQ. (50)

α	ζ	s^*	α	ζ	s^*
0.0	1.317		0.576	0.7	1.215
.1	1.296	12.96	.634	.6	0.946
.2	1.232	6.16	.692	.5	.723
.3	1.130	3.76	.751	.4	.533
.4	0.992	2.48	.812	.3	.370
.5	.831	1.662	.873	.2	.229
.519	.8	1.541	.936	.1	.107
			1.000	.0	.000

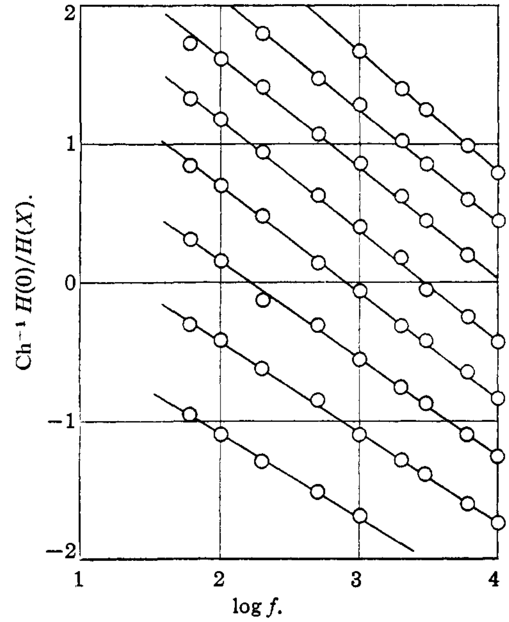

Fig. 1.—Test plots for *p*ViCl-Ph$_2$; 80:20 at 5° intervals; lowest curve 35°, highest 70°.

For example, a value of α = 0.42 gives s^* = 2.303 by interpolation in Table I; in other words, $F(s)$ drops to one-half its peak value in the first decade of τ-values above or below the value of τ corresponding to maximum H when α = 0.42. The area under $F(s)$ between the limits $\pm s^*$ accounts for a large fraction of the total integral, and is not very sensitive to α: for α = 0.1, the integral of $F(s)$ between $\pm s^*$ is 0.635, for α = 0.5 is 0.587, and for α = 0.9 is 0.505.

The value x^* satisfying

$$H(x^*)/H(0) = 1/2$$

is very simple to find: it corresponds to

$$x^* = \cosh^{-1} 2 = 1.317 \qquad (54)$$

For x^* = 2.303, α = 0.572; that is, for H to drop to one half its peak value in one decade of frequency above or below f_m requires a distribution parameter equal to 0.572. For α = 0.42, the example of the previous paragraph, x^* = 3.14; in other words, the H-curve is always blunter than the F-curve for the same value of α.

For comparison with experiment, it is useful to have some values of the integral $J(x)$ defined by (17) and (26). With the explicit form (44) for $F(s)$ which is derived from the empirical form (43) of $H(x)$, it was not found possible to carry out the integration in closed form, except for certain rational values of cos $\pi\alpha/2$. These results are summarized in the following list of equations: details of computation are omitted in order to save space.

Let $J(\alpha, x)$ be the value of $J(x)$ for a given value of α. Then it can be shown that

$$J(\alpha, 0) = 1/2 \qquad (55)$$

$$J(\alpha,x) + J(\alpha, -x) = 1 \qquad (56)$$

$$J(\alpha,\infty) = 1;\ J(\alpha,0) = 0 \qquad (57)$$

$$J(0,x) = 1/2$$

$$J(1/3,x) = \frac{1}{1+e^{-2x}} - \frac{2}{\sqrt{3}}\frac{\sinh(x/3)}{2\cosh(2x/3) - 1} \qquad (58)$$

$$J(1/2,x) = \frac{1}{1-e^{-2x}} - \frac{1}{4\sinh(x/2)} \qquad (59)$$

$$J(1,x) = 1/(1+e^{-2x}) \qquad (60)$$

The following table of formulas gives the slopes of the $J - x$ curves at the midpoints, where $x = 0$.

$$[\partial J(0,x)/\partial x]_{x=0} = 0 \qquad (61)$$

$$[\partial J(1/3,x)/\partial x]_{x=0} = 1/2 - 2\sqrt{3}/9 \qquad (62)$$

$$[\partial J(1/2,x)/\partial x]_{x=0} = 9/48 \qquad (63)$$

$$[\partial J(1,x)/\partial x]_{x=0} = 1/2 \qquad (64)$$

Some discussion of Equations (55)–(64) seems appropriate. The function $J(x)$, which is closely related to the dielectric constant (*cf.* Eq. 22) is a symmetrical sigmoid through the point (1/2,0), going asymptotically to zero for infinite frequency as $\epsilon' \longrightarrow n^2$ and to unity for zero frequency as ϵ' approaches the static dielectric constant. The inflection slope is $^1/_2$ for the case of a single time of relaxation ($\alpha = 1$) and decreases to zero as the limit of an infinitely wide distribution ($\alpha = 0$) is reached. For $\alpha \leqslant 0.3$, the J–x curve is practically linear, over a fairly wide range of frequency near $x = 0$, which is in agreement with the approximate linearity of the ϵ'–$\log f$ curves reported for polyvinyl chloride–tricresyl phosphate systems.[11]

V. The Average Moment of a Polymer Molecule.—Let us consider a long chain polymer of the type $(\text{—CH}_2\text{CHCl—})_n$, containing n monomeric units. Assume that all polymeric molecules in the system have the same chain length. Neglect interaction of neighboring chains, by assuming the polymer present in dilute solution in a non-polar solvent. Then we know from the work of Mark and Kuhn[4,5] that a long chain molecule is curled up, rather than extended, with an average length proportional to the square root of n. Let μ be the dipole moment of the chain molecule in a particular configuration, and $\bar\mu$ be the vector sum of μ and the moment induced by the molecule in its environment. Let $(\mu\cdot\bar\mu)_{av}$ be a mean value taken over all configurations of the chain permitted by free rotation at each C–C bond. This average will include certain configurations which require an (impossible) interpenetration of the chain. We shall also neglect dipole–dipole interaction between different segments of the same chain for the present. Later we hope to treat more complicated models, and to remove some of the approximations involved in this calculation, which is to be considered as a first approximation.

We can now define an average moment $\tilde\mu$ per monomer unit as follows

$$\tilde\mu = \sqrt{(\mu\bar\mu)_{av}/n} \qquad (65)$$

It will be derivable from experimental data if we determine $P_2'(0)$ as outlined in Section IV.

Let k and l be two arbitrarily selected dipoles along the chain and γ_{kl} be the angle between the individual C–X dipoles μ_k and μ_l in a specified configuration and let $\overline{\cos\gamma_{kl}}$ denote the average of the cosine taken over all configurations obtained by rotations which preserve tetrahedral bond angles. It is obvious that only rotations at bonds *between* μ_k and μ_l can affect $\overline{\cos\gamma_{kl}}$; as k and l are given all possible values, all chain configurations will be included. For μ, the total moment of the chain molecule, we then have

$$\mu = \sum_k \mu_k$$

and for

$$(\mu\bar\mu)_{av} = \overline{\mu^2}$$

$$\overline{\mu^2} = n\,\mu_0^2(1 + S_n) \qquad (66)$$

where

$$n\,S_n = \sum_{k=1}^{n}\sum_{l\neq k}\overline{\cos\gamma_{kl}} \qquad (67)$$

and μ_0 is the moment of a C–X group in free space. Combining with (65), we find

$$\tilde\mu = \mu_0\sqrt{1 + S_n} \qquad (68)$$

By a method similar to the one suggested by Eyring[12] we find

$$\lim_{n\rightarrow\infty} S_n = S = -2\beta/(1 - \beta) \qquad (69)$$

where $\beta = {}^1/_9$, the square of the cosine of the tetrahedral angle.[13]

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(11) Fuoss, This Journal, **60**, 451 (1938).

(12) Eyring, *Phys. Rev.*, **39**, 746 (1932).

(13) The details of the calculation are as follows. Neglecting the effect of end groups, there are $2n$ C–C bonds and n C–Cl bonds. Let $\mathbf{a}_{2l}$ be a unit vector in the direction of the l-th C–Cl bond, $\mathbf{a}_{2l+1}$ a unit vector from that carbon to its nearest neighbor, and so on until $\mathbf{a}_{2k+1}$ is the unit vector between the carbon next to the $2k$-th one, holding the k-th Cl-atom, and let $\mathbf{a}_{2k}$ be a unit vector in the direction of the k-th C–Cl bond. Then

$$\mu_k = \mu\mathbf{a}_{2k} \text{ and}$$

$$\mu_l = -\mu\mathbf{a}_{2l}$$

The value of $\cos\gamma_{kl}$ is then given by

$$\cos\gamma_{kl} = -\mathbf{a}_{2k}\cdot\mathbf{a}_{2l}$$

and in order to obtain its average, we must average over rotation at all of the bonds between k and l.

If $\mathbf{b}_j$ and $\mathbf{c}_j$ are mutually perpendicular unit vectors perpendicular to $\mathbf{a}_j$, we have $\mathbf{a}_{2k} = \cos\gamma_0\,\mathbf{a}_{2k-1} + \sin\gamma_0\cos\varphi_{1k}\,\mathbf{b}_{2k-1} + \sin$

Substituting (69) in (68), we obtain

$$\bar{\mu} = \sqrt{3}\,\mu_0/2 \qquad (70)$$

The significance of (70) is that the average moment per monomer unit is $\sqrt{3}/2 = 0.866$ of its value as a gas molecule; the decrease is due to components of different moments being brought anti-parallel by the convolutions of the chain.

VI. **Comparison with Experiment.**—We shall consider first the empirical interpolation formula (43) for $H(x)$. The test was made on the data for the system polyvinyl chloride–diphenyl, which were reported in the two previous papers of this series.[3] First ϵ'' was plotted against $\log f$ in order to determine ϵ''_m, and then the dielectric constant ϵ'_m for f_m was interpolated on an $\epsilon' - \log f$ plot. (The latter is not very accurately determined at this stage of the calculation, because the $\epsilon'' - \log f$ plots, while determining ϵ''_m very accurately, leave $\log f_m$ somewhat doubtful on account of the bluntness of the curves. This inaccuracy is harmless, however, because ϵ' enters $H(x)$ only as a small term.) For temperatures where ϵ''_m was not included in the experimental frequency range, empirical free-hand extrapolations were made on $\epsilon''_m - t$ plots. These values become, of course, steadily more doubtful the greater the extrapolation, but the results are included for use in discussion. Having determined ϵ''_m and ϵ'_m, the function

$$\epsilon''_m(2 + 1/\epsilon'^2_m)/\epsilon''(2 + 1/\epsilon'^2) \qquad (71)^*$$

was computed, and then the number which had (71) as its hyperbolic cosine[14] was plotted against log frequency. In all cases tested, straight lines were obtained; an example is shown in Fig. 1 for the system pViCl–Ph$_2$, 80:20 over the temperature range 35–70°. The linearity of these plots verifies the equation

$$H(x) = H(0)\ \mathrm{sech}\ \alpha x \qquad (72)$$

and α the distribution parameter is obtained as 0.434 times the slope of the line. Also $\log f_m$ is very accurately determined by the intersection of the line with the axis $\mathrm{ch}^{-1}(H_m/H_0) = 0$.

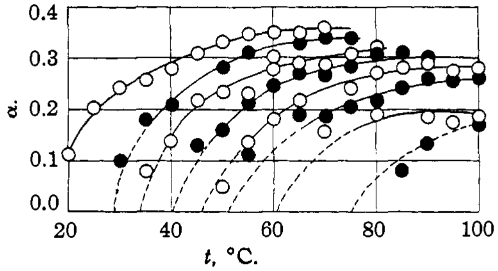

Fig. 2.—Distribution parameter as a function of composition and temperature for 20, 15, 12, 9, 6, 3, 1 and 0% diphenyl with polyvinyl chloride to make 100%. Curve at upper left is for 80:20; curve at lower right is for pure polyvinyl chloride.

In Fig. 2 are plotted values of α as functions of temperature for different compositions containing 0–20% diphenyl, 100–80% polyvinyl chloride. For a given composition, the distribution parameter increases regularly with increasing temperature, and apparently reaches an asymptotic value. This value might well correspond to the case where thermal agitation is sufficient (kT large enough) so that interaction between neighboring chains has become negligible. When the chains are independent, times of relaxation due to chain interaction will be lacking, and obviously a sharper distribution (larger α) will result.

The decrease of α toward lower temperatures is also very interesting. It has been shown previously[3] that a transition temperature of the nature of an internal freezing point appears in polymeric systems, below which chain-to-chain coupling seems to predominate. (We recall that the temperature coefficient of the low temperature ϵ'' maximum gave an energy of about 2.5 kcal. as contrasted to 30–50 kcal. for the high temperature maximum.) A value of $\alpha = 0$ corresponds to an infinitely wide distribution of relaxation times which would correspond to a high coupling between neighboring chains, so that the whole sample behaved like one giant molecule. Before

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$\gamma_0 \sin \varphi_{2k}\, \mathrm{c}_{2k-1}$ where γ_0 is the bond angle and φ_{2k} is the angle in the b-c plane made by the projection of a. If we average over all values of φ, which corresponds to free rotation at the first bond, we obtain

$$\overline{\mathrm{a}_{2k}} = \cos^2 \gamma_0\, \mathrm{a}_{2k-1}$$

If now we project a_{2k-1} onto a_{2k-2}, and average over rotation at this bond, we similarly obtain

$$\overline{\overline{\mathrm{a}_{2k}}} = \cos^2 \gamma_0\, \mathrm{a}_{2k-2}$$

Finally, if we average over rotation at all the bonds between μ_k and μ_l, we obtain simply

$$\overline{\cos \gamma_{kl}} = -\cos^{2|k-l|} \gamma_0$$

Using the abbreviation

$$\beta = \cos^2\gamma_0$$

S_n becomes

$$S_n = -\frac{1}{n}\sum_{k=l}^{n}\left\{\sum_{l=k+1}^{n} \beta^{l-k} + \sum_{l=1}^{k-l} \beta^{k-l}\right\}$$

On evaluating the geometric sums, we find

$$S_n = -\frac{2\beta}{1-\beta}\left(1 + \frac{1}{n}\,\frac{\beta^n - 1}{1-\beta}\right)$$

Assuming that n is very large compared to unity, we obtain (69)

$$S = \lim_{n\to\infty} S_n = -2\beta/(1-\beta)$$

(14) "Smithsonian Mathematical Tables, Hyperbolic Functions," Fourth Reprint, Washington, 1931.

any calculations reported in this paper were made, the internal melting points t_0 of the polyvinyl chloride–diphenyl systems were determined empirically from the shape of the ϵ''–T curves and the speed with which temperature equilibrium was obtained.[3] It, therefore, seems significant that smooth curves (dotted in Fig. 2) can be drawn connecting the α–t curves and the points (0–t_0) for these systems.

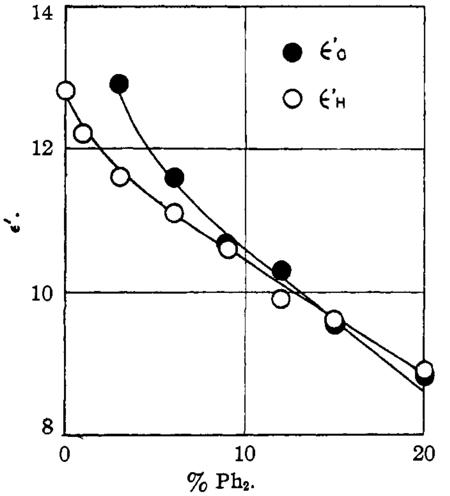

Fig. 3.—Static dielectric constants for the system polyvinyl chloride–diphenyl.

For a given temperature, the value of α increases as we increase the concentration of diphenyl. This change is what would be expected if the effect of the plasticizer is to separate chains and permit them greater freedom to curl up. If the estimated asymptotic values of α for high temperatures are plotted against composition, the most rapid change occurs in the range 0–5% diphenyl. This result supports the previous conclusion[3] that the first plasticizer added is most effective in breaking chain-to-chain coupling; after that, it acts more as a mere volume diluent.

We next turn to a consideration of the static dielectric constants. Having determined α by the graphical method outlined above, we calculate Z by (47), and φ (ϵ_0) by (16) and solve (13) for ϵ_0, using $n^2 = 2.4$. (The indices of refraction for the 0–20% diphenyl systems ranged from 1.53 to 1.57; for simplicity the average was used in numerical calculations.) For temperatures above that corresponding to the 60 cycle maximum in ϵ'' (*i. e.*, well above the internal melting point), the calculated ϵ_0 values showed a slow decrease with increasing temperature, as might be expected from decreasing density. Below this temperature range, however, the calculated values of ϵ_0 increased rapidly with decreasing temperature. Until more experimental data are available, it is impossible to say whether this effect is real, or whether it is due to the uncertainty in the extrapolated ϵ''_m values which were used in the calculation. For temperatures below the transition, we naturally expect low static dielectric constants.

In Fig. 3 are plotted the values of ϵ_0 at the temperature of the 60-cycle maximum in ϵ'' as a function of composition for the pViCl–Ph_2 systems. For comparison, the ϵ_H values obtained by an empirical method[3] based on an assumed viscosity mechanism are included in Fig. 3. The good agreement in the range of higher diphenyl concentrations confirms a number of the previously made conclusions regarding the mechanism of a. c. absorption in polar polymers.

Another result contained in our calculations is that we should be able to predict the dielectric constant curve from the loss factor curve. For example, the value ϵ'_m of ϵ' at the frequency of maximum in H is given by

$$J(\alpha,0) = 1/2 = [2\epsilon'_m - 1 - 1/\epsilon' - \varphi(n^2)]/9Z \quad (73)$$

Very good agreement between calculated and observed values was obtained in the high temperature range, where effects due to chain interaction were apparently negligible. At lower temperatures, the calculated values were, as expected, too small. Still more interesting are the inflection slopes of the ϵ'–log f plots, or what is essentially the same thing, the slopes of the J–x plots. In Fig. 4 the solid curve is the theoretical $(\partial J/\partial x)_{x=0}$ curve as a function of α; it was calculated by Equations (61)–(64). The points are chord slopes of the experimental J–x plots at $f = f_m$. It will

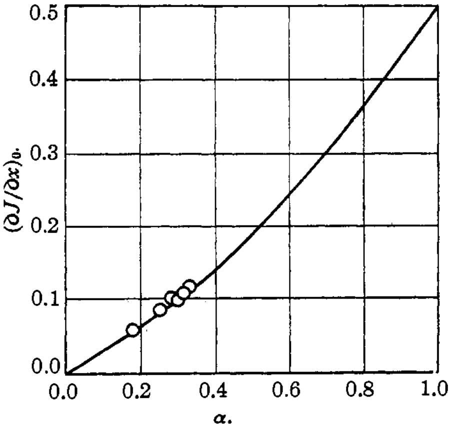

Fig. 4.—Inflection slopes of $J - x$ curves: curve calculated, circles observed.

be noted that the decreasing inflection slope as the concentration of polymer increases follows exactly the predicted decrease with the observed decrease in α not only in general trend but also in absolute value. We emphasize that these calculations of dielectric constants and slopes are based on determinations of the loss factors. The agreement proves at least that our picture is self-consistent in that knowledge of one component of the a. c. vector permits calculation of the other.

Having obtained values of the static dielectric constants, we are now able to calculate average moments per monomer unit by means of (11) and (14). We have

$$P'_2(0) = Z_0V/x_2 \qquad (74)$$

where

$$9Z_0 = \varphi(\epsilon_0) - \varphi(n^2) \qquad (75)$$

and

$$\bar{\mu} = 0.0127\sqrt{P'_2(0)\cdot T} \qquad (76)$$

The results of these calculations for the pViCl–Ph_2 systems are summarized in Fig. 5. As could be expected from the behavior of the static dielectric constant, the mean moments per monomer unit increase with decreasing diphenyl concentration at a given temperature, and for a given composition, start to increase very rapidly as the temperature starts to approach the transition temperature. For each composition, however, an asymptotic value independent of temperature is apparently reached, which gives confidence in the opinion that we are dealing with a real moment. If we plot the estimated asymptotic values of the moments against composition (Fig. 6), we find for the (—CH_2·CHCl—) unit a limiting value of $\bar{\mu} \approx$ 2.0. According to tables of moments[15] we estimate μ_0 of Eq. 70 to be 2.0 (the moment for ethyl chloride, for example, is given as 1.99). The theoretical value of $\bar{\mu}$ is accordingly $\sqrt{3}$ = 1.7. Considering the various assumptions involved, we consider the agreement satisfactory. Several explanations of the discrepancy may be pointed out. In the first place, our lowest concentration is 80% polymer, and while this is a very low *molar* concentration, it is still a high *volume* concentration. More data at lower concentrations of polymer are obviously needed. In the second place, an assumption made in the theoretical calculation is incorrect: configurations involving chain interpenetration were included in the average, and the theoretical result thus calls for more cancellation of moments than can occur in the real molecule.

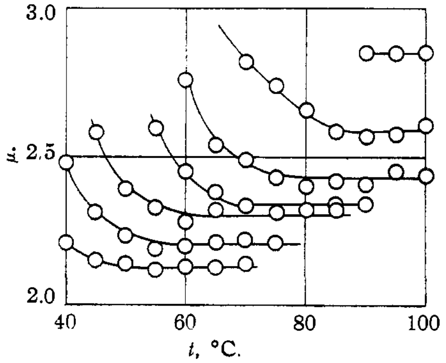

Fig. 5.—Dipole moments as functions of temperature and composition for 20, 15, 12, 9, 6, 3 and 1% diphenyl with polyvinyl chloride to make 100%. Curve at upper right is for 1%; curve at lower left for 20%.

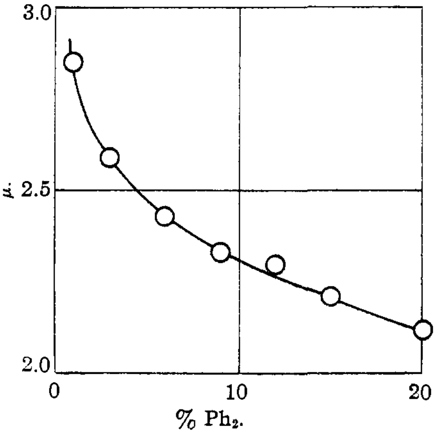

Fig. 6.—Moments of monomer unit as function of concentration.

We finally consider the distribution function. If we compare it with the Wagner distribution, we see the reason for the systematic deviations encountered in applications of the Gauss function to data on polyvinyl chloride. The asymptotic form of the function derived by Fourier transform from the experimental loss factor curve is $[\alpha \cos(\alpha\pi/2)/\pi]e^{-\alpha s}$ while the Gauss function is $(b/\sqrt{\pi})e^{-b^2s^2}$. Since we must always have $\int_0^\infty G(\tau)\mathrm{d}\tau = 1$, the more rapid decrement of the Gauss function for large values of s as compared the much slower decrement of $F(s)$ can only mean that near $x = 0$, the Gauss function gives values which are too large. In other words, the Gauss function weights times of relaxation near the most probable one too heavily, while the curve obtained from the data calls for a still broader distribution. A theoretical investigation of the expected form of the distribution function will be made in a later

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[15] Smyth, "Dielectric Constant and Molecular Structure," A. C. S. Monograph, Reinhold Publ. Corp., New York, N. Y., 1930.

paper, in which the internal rotatory diffusion of long chain molecules will be treated.[16]

Summary

1. A method is given whereby the distribution of times of relaxation of a polar system can be calculated from the observed loss factor–frequency curve.

2. The reduced polarization is introduced as a simplification in calculating a. c. properties of polar systems.

3. Experimental loss factor–frequency curves for systems containing polyvinyl chloride can be represented empirically by the approximate equation

$$\epsilon'' = \epsilon''_m \operatorname{sech} [\alpha (\ln f/f_m)]$$

where α is the distribution parameter.

4. The average moment per monomer unit of a linear polar polymer of the type $(\text{—CH}_2\cdot\text{CHX—})_m$, assuming free rotation, is found to be $\sqrt{3}\,\mu_0/2$, where μ_0 is the moment of the equivalent group in free space.

5. Application of the theoretical results to data on polyvinyl chloride–diphenyl systems gives a value of 2.0 to the C–Cl moment in polyvinyl chloride.

6. Previous empirical conclusions concerning chain interaction in polymeric systems receive further support from the present theoretical treatment.

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[16] Relations between the real and imaginary parts of the dielectric constant similar to those presented here have been discussed by Kronig, *J. Optical Soc. Am.*, **12**, 547 (1926), and Kramers, *Atti Congr. dei Fisici, Como*, 545 (1927). Their use in connection with magnetic relaxation phenomena is treated by Gorter and Kronig, *Physica*, **3**, 1009 (1936).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YENCHING UNIVERSITY]

Solubility Studies. II. The Activity Product and Standard Electrode Potential of Silver Iodate from 10 to 35°

BY NORMAN C. C. LI AND YING-TU LO

In the first part of this series[1] it was shown that the heat of solution and standard electrode potential of silver chromate derived with the aid of solubility data for silver chromate agree closely with the values determined directly from calorimetric and potential measurements. This paper describes solubility determinations with silver iodate in solutions of potassium nitrate from 10 to 35°. The experimental values are compared with those calculated from the Debye–Hückel equation and the activity product of silver iodate is combined with the standard potential of the silver electrode to obtain the standard potential of the Ag(s), $AgIO_3$(s), IO_3-electrode at 10, 20, 25, 30 and 35°.

Experimental

Silver iodate was prepared by mixing dilute solutions of c. p. silver nitrate and twice-recrystallized potassium iodate. The finely-divided precipitate obtained was aged for several days in the mother solution, washed repeatedly with conductivity water and dried in a vacuum oven at 60°. The potassium nitrate solutions, used as solvents, were prepared by weight directly from thrice-recrystallized salt, followed by proper dilutions for the various concentrations.

The solubility determinations were carried out as described by Kolthoff and Lingane[2] using brown glass bottles, coated inside with paraffin and closed with paraffined corks. The temperature was regulated to ±0.05° for each temperature and three determinations were made for each point of the reported solubility curves.

The analysis of the saturated solutions consisted in the iodimetric determination of the iodate in 100-ml. samples by means of 0.01 *N* sodium thiosulfate solutions, using a calibrated microburet. The sodium thiosulfate solutions were standardized frequently against pure potassium dichromate and appropriate corrections made for blanks in each case. The titrations were accurate to ±0.3%.

Results

The data obtained are listed in Table I. The first column gives the molarity m of potassium nitrate, the second the solubility s in moles per liter averaged, in each case, from three closely agreeing results; the third column lists the square root of the ionic strength assuming that all the substances are completely ionized.

Using the Debye–Hückel equation in the form

$$\log f_{\pm} = -B\sqrt{\mu}/1 + A\sqrt{\mu} \qquad (1)$$

in which the activity coefficient

$$f_{\pm} = S_0/S_{\mu} \qquad (2)$$

the following equation can be obtained

$$\log S_0 - \log S_{\mu} = -B\sqrt{\mu}/1 + A\sqrt{\mu} \qquad (3)$$

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[1] Li, *J. Chinese Chem. Soc.*, in press.

[2] Kolthoff and Lingane, *J. Phys. Chem.*, **42**, 133 (1938).