Fig. 6.—Dependence of 60 cycle dielectric constant on d. c. conductance.

Fig. 7.—Dependence of 60 cycle loss factor on d. c. conductance.

this will permit a study of electrolytic conductance in the range of very high viscosities ($\eta \sim 10^6$ poises).

Summary

1. The electrical properties of polyvinyl chloride plastics depend on thermal history. Increased time and temperature of heating give increased d. c. conductance.
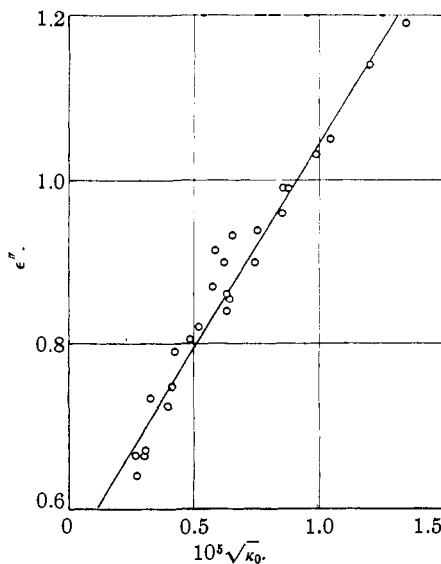
2. The amount of pyrolysis can be followed by adding a soluble lead compound such as lead abietate to the plasticizer and determining the conductance for various heating times and temperatures.

3. The dielectric constant changes with time in a way which suggests a relaxation mechanism.

4. There is a one to one correlation between d. c. conductance, dielectric constant and loss factor.

SCHENECTADY, N. Y.   RECEIVED JUNE 3, 1939

Electrical Properties of Solids. V. Their Variation at 40° with Frequency and Composition in the System Polyvinyl Chloride–Tricresyl Phosphate

BY RAYMOND M. FUOSS

I. Introduction

Polyvinyl chloride as ordinarily obtained is an amorphous white powder, which can be converted under hydraulic pressure at 120° into a transparent brittle solid. By the addition of various liquids, such as tricresyl phosphate, it can be softened or "plasticized," to give solids ranging from glass-like to jelly-like substances, going through a tough rubber-like form at about 35–45% plasticizer. Dilute solutions of the polymer in plasticizers are very viscous liquids. The two-phase system polymer–plasticizer thus permits a study of electrical properties over an enormous range of macroscopic viscosity. By varying the chemical nature of the two components, or by adding a third, a wide range of conductance and dielectric constant can then be investigated.

In previous papers in this series, experimental methods[1] for obtaining electrical data of reasonable precision on solids have been described, and a preliminary account of some of the properties of the system polyvinyl chloride–tricresyl phosphate

(1) (a) Fuoss, THIS JOURNAL, 59, 1703 (1937); (b) 60, 451 (1938); (c) 60, 456 (1938); (d) 61, 2329 (1939).

TABLE I

DIELECTRIC CONSTANTS OF POLYVINYL CHLORIDE–TRICRESYL PHOSPHATE PLASTICS AT 40°

Polyvinyl chloride, %	Frequency								
	20 ~	60 ~	120 ~	250 ~	500 ~	1000 ~	2000 ~	5000 ~	10,000 ~
100	3.454	3.435	3.419	3.397	3.370	3.338	3.306	3.263	3.231
95	3.300	3.268	3.257	3.239	3.223	3.204	3.182	3.154	3.132
90	3.320	3.275	3.250	3.225	3.195	3.170	3.145	3.115	3.085
85	3.640	3.510	3.440	3.375	3.320	3.270	3.220	3.165	3.120
80	4.760	4.395	4.190	4.010	3.840	3.695	3.580	3.425	3.310
75	6.50	5.87	5.48	5.10	4.79	4.50	4.23	3.88	3.64
70	8.29	7.56	7.10	6.62	6.17	5.72	5.27	4.67	4.21
65	9.47	9.02	8.64	8.14	7.65	7.14	6.62	5.82	5.24
60	10.00	9.69	9.42	9.08	8.62	8.32	7.78	6.97	6.37
55	10.33	10.00	9.80	9.59	9.37	9.09	8.75	8.08	7.57
50	10.46	10.19	10.02	9.85	9.68	9.50	9.25	8.76	8.30
45	10.45	10.21	10.06	9.90	9.75	9.60	9.40	9.06	8.70
40	10.38	10.18	10.05	9.92	9.80	9.65	9.48	9.22	8.97
35	(12.25)	(11.00)	(10.38)	(10.88)	9.55	9.40	9.28	9.08	8.86
20	....	8.99	....	....	8.90	8.72	..	..	..
0	....	6.92	....	....	6.89	6.89	..	..	..

TABLE II

LOSS FACTORS OF POLYVINYL CHLORIDE–TRICRESYL PHOSPHATE PLASTICS AT 40°

Polyvinyl chloride, %	Frequency							
	20 ~	60 ~	120 ~	250 ~	500 ~	1000 ~	2000 ~	5000 ~
100	0.031	0.040	0.046	0.053	0.060	0.066	...	...
95	.033	.035	.035	.037	.038	.040	0.042	...
90	.060	.058	.056	.054	.052	.049	.045	...
85	.133	.131	.127	.124	.116	.107	.097	0.079
80	.451	.441	.405	.368	.330	.294	.256	.208
75	.752	.810	.778	.726	.664	.598	.530	.440
70	.920	.978	.994	.992	.972	.930	.880	(.820)
65	.720	.836	.904	.976	1.056	1.090	1.084	1.080
60	.550	.630	.686	.770	0.860	0.952	1.040	1.160
55	.45	.46	.49	.55	.63	.71	0.82	0.98
50	.37	.38	.40	.45	.51	.60	.70	.85
45	.3	.345	.3	.30	.34	.38	.44	.55
40	...	.348	...	.27	.29	.30	.32	....
35	...	1.39	1.05	.80	.60	.45	.35	....

has been presented.[1b] This paper represents the first part of a systematic study of the properties of plastic solids. The conductance and dielectric constant have been determined at 40° over the frequency range 20 to 10^4 cycles (low voltage[1c]) for the system polyvinyl chloride–tricresyl phosphate, over the entire concentration range.

II. Experimental Methods

Cells, bridges, materials, method of preparing and measuring samples and experimental precautions already have been described.[1,2]

Milling was the minimum necessary for thorough mixing, and pressing was only ten minutes at 120°. By using mild thermal conditions in the preparation of this series of samples, pyrolysis of the polyvinyl chloride was kept small, so that the accompanying d.c. conductance due to hydrogen

(2) Fuoss, Trans. Electrochem. Soc., **74**, 91 (1938).

chloride from pyrolysis would not be too serious a disturbing factor.

III. Results

Measurements were made at a number of frequencies between 15–20 cycles and 10 kilocycles. In order to save space in presentation, values of dielectric constant ϵ' and a. c. loss factor ϵ'' have been interpolated from the data to round frequencies in the above range, and are given in Tables I and II. The d. c. conductance was also measured; these values are summarized in Table III.

The a. c. loss factor is defined as

$$\epsilon'' = 18 \times 10^{11} (\kappa - \kappa_0)/f \qquad (1)$$

where κ is the conductance at frequency f and κ_0 is the electrolytic conductance as measured on a d. c. bridge. It is assumed, for the present, that κ_0 is independent of frequency.

TABLE III

D. C. CONDUCTANCES OF POLYVINYL CHLORIDE–TRI-
CRESYL PHOSPHATE PLASTICS

Polyvinyl chloride, %	$\kappa \times 10^{10}$	Polyvinyl chloride, %	$\kappa \times 10^{10}$
90	0.001	55	0.198
85	.010	50	.510
80	.014	45	1.462
75	.025	40	3.23
70	.028	35	3.63
65	.014	20	12.40
60	.064	0	0.75

Densities were determined by weighing the samples and measuring their dimensions with vernier scales. For the 60 polyvinyl chloride–40 tricresyl phosphate samples some densities were also determined by weighing under water; the two methods checked within several tenths of one per cent., the experimental precision of the former method. As nearly as we can conclude from the data, polyvinyl chloride and tricresyl phosphate mix to form a plastic without volume change.
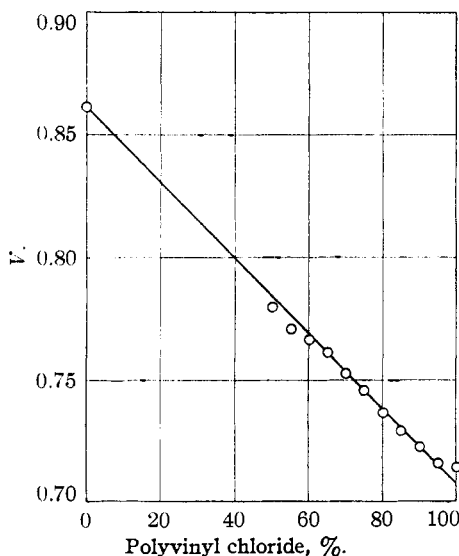
Fig. 1.—Specific volumes of polyvinyl chloride–tricresyl phosphate plastics.

In Fig. 1 the specific volume is plotted against composition by weight; the circles are observed and the solid line is that corresponding to

$$v = p_1 v_1 + p_2 v_2 \qquad (2)$$
$$p_1 + p_2 = 1 \qquad (3)$$

where $v_1 = 0.706$ and $v_2 = 0.861$ cc./g. are, respectively, the specific volumes of pure polyvinyl chloride and of tricresyl phosphate. This result is in accord with Brönsted's view[3] that all solu-

(3) Brönsted, Compt. rend. trav. Lab. Carlsberg, Sér. chim., 22, 99 (1937).

tions of high polymers are very dilute solutions from the thermodynamic point of view, on account of the enormous molecular weight of the polymer.

IV. Discussion

In general, most polar substances show a high dielectric constant at low frequencies, and a small dielectric constant approaching the square of the index of refraction at high frequencies. The transition from high to low values usually occurs over a fairly narrow range of frequency; about 90% of the inflection region of the ϵ'–f curve lies within two decades of frequency. In this frequency range, the loss factor goes through a maximum, and approaches zero for higher or lower frequencies. The plastic solid, as exemplified by the system under discussion here, shows a markedly different behavior. The dielectric constant decreases (Fig. 2) with increasing frequency,
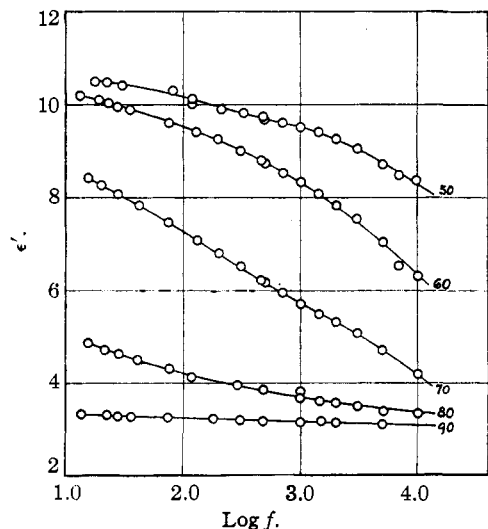

Fig. 2.—Dependence of dielectric constant on frequency and composition.

but only very slowly as compared to normal polar systems. The loss factor shows a maximum (Fig. 3) in the range 80–65% polyvinyl chloride within our present frequency range, which is nearly three decades wide, but is still relatively far from zero at the extreme frequencies. In other words, the plastic system roughly resembles ordinary systems in that the dielectric constant decreases with increasing frequency, and the loss factor has a maximum at some definite frequency (for a given temperature), but differs from them in the width of the dispersion region. The inflection slope on an ϵ'–f plot is much shallower for the plastic, and the ϵ'' maximum is very much broader.
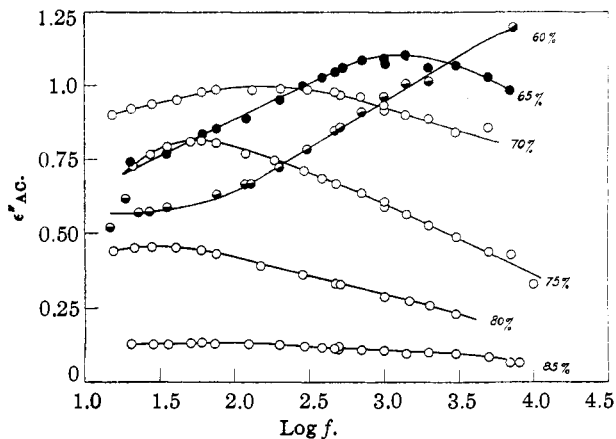
Fig. 3.—Dependence of loss factor on frequency and composition.

If a much wider range of frequency were available, an S-shaped $\epsilon'-f$ curve would probably have been obtained for all the systems of Table I. As it is, those containing between 90 and 70% polyvinyl chloride give concave-up ϵ'–log f curves in the range 0.01–10 kc. (inflection at lower frequencies). The 70% sample gives a practically linear ϵ'–log f curve, which indicates an inflection point within this range of frequency (at about 150 cycles, judging from the maximum in the ϵ''–log f curve). Those containing less than 70% polyvinyl chloride give curves that are concave-down, which suggests that their inflection points lie at higher frequencies than 10 kc. The loss factor curves similarly show a shift of the absorption maxima to higher frequencies as the plasticizer content increases.

Another reversal in curvature appears near the pure polyvinyl chloride end of the composition range. Pure polyvinyl chloride gives a concave-
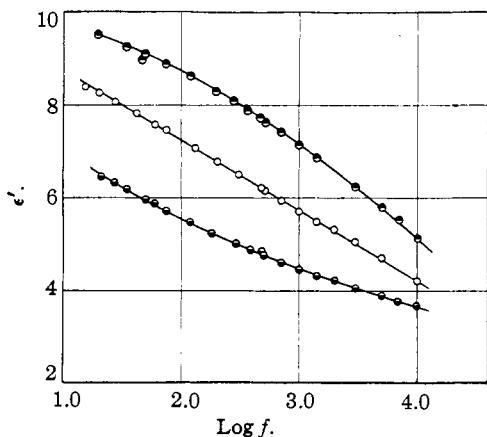
down ϵ'–log f curve, and an ϵ''–log f curve which rises with frequency in the 0.01–10 kc. range, indicating a center of dispersion at higher frequencies than 10 kc. The addition of 5% tricresyl phosphate decreases the dielectric constant, converts the ϵ'–log f curve almost to a straight line and decreases the rate of increase of ϵ'' with frequency; the center of the dispersion is therefore at lower frequencies than for the 100% sample, although still beyond 10 kc. At 10% plasticizer, the ϵ'–log f curve is nearly linear, and ϵ'' now decreases with increasing frequency in the experimental range, corresponding to a center of dispersion *below* 10 cycles. At 15% tricresyl phosphate, the center of dispersion appears to be just about at 10 cycles. Then with increasing plasticizer, the dispersion moves regularly to higher frequencies. The critical region between 95 and 85% polyvinyl chloride, where the dispersion crosses the frequency band from high to low frequencies and back again, will require further study.

Attention has already been called to the bluntness of the absorption maxima and the width of the dispersion on a frequency scale. There is further experimental evidence that the dispersion is much broader than can be shown by actual a. c. measurement by our present methods. If the
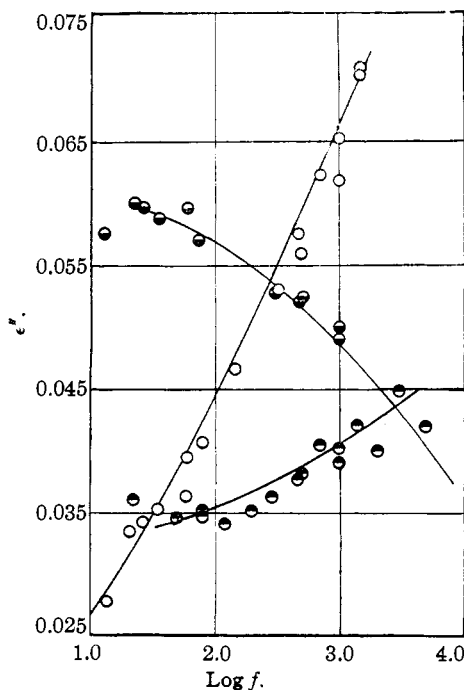

Fig. 4.—Transition region in dispersion—polyvinyl chloride: ●, 65%; ○, 70%; ◓, 75%.

Fig. 5.—Loss factor in high polymer plastics: ○, 100%; ◑, 95%; ◓, 90%.
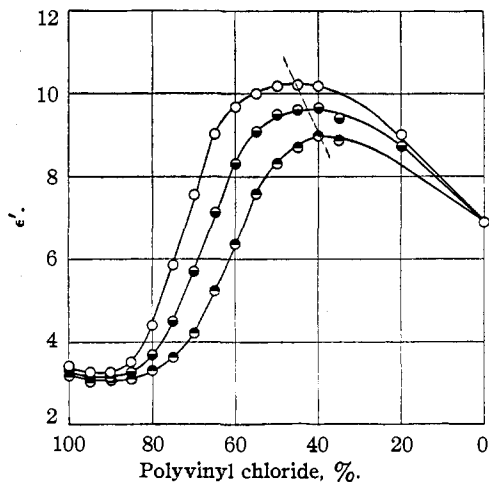
Fig. 6.—Dependence of dielectric constant on composition: $\bigcirc$, 60~; $\ominus$, 1000~; $\ominus$, 10 kc.

Fig. 7.—Dependence of loss factor on composition: $\bigcirc$, 60 ~; $\bullet$, 1000 ~.

observed conductance is plotted against frequency for the samples of Table II, approximate straight lines are obtained *which extrapolate linearly to the d. c. conductance.*[1b] Even for those samples for which a maximum in ϵ'' was found, the per cent. change in ϵ'' was nevertheless small; the fact that the a. c. data extrapolate *linearly* to the d. c. conductance (*cf.* eq. 1) is equivalent to saying that ϵ'' will not change much with frequency until extremely low frequencies are reached. On the basis of any of the present theories of absorption, ϵ'' must reduce to zero at zero frequency; *i. e.*, the κ–f plots must approach κ_0 with a horizontal tangent in the limit. No evidence of curvature was observed at 40°; at higher temperatures, the κ–f curves do, however, become concave-up in the low (10–100 cycles) frequency range.

A number of possible explanations of the width of the dispersion have been suggested, but no general theory with only a small number of arbitrary constants with assignable physical significance has been advanced. The fundamental difference between a solution of simple dipole molecules such as ethyl chloride and a plastic containing polyvinyl chloride is, aside from the obvious difference in viscosity, the fact that the ethyl chloride molecules are free to assume a normal distribution of orientations in thermal equilibrium, while the dipoles of polyvinyl chloride are constrained to fluctuations about orientations fixed by the accidental convolutions of the chain molecule which carries them. The components of moment in the direction of the field are thus subject to a different distribution law than for
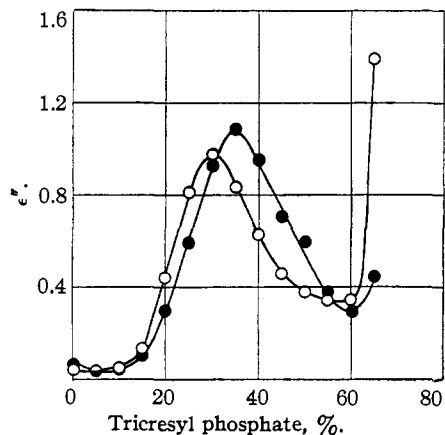
free dipoles. An eventual theory of the electrical properties of dipolar polymers must include explicitly this influence of structure on distribution.

The influence of such a distribution on the a. c. absorption can be qualitatively described. Under the action of the field, adjacent parts of the same or different chain molecules can be irreversibly twisted into new positions, in much the same way as elastic strains relax in the plastic. This process corresponds to a loss factor independent of frequency. If a second frequency-sensitive absorption (Debye relaxation or Maxwell–Wagner polyphase dielectric) were also present, curves like those of Fig. 3 would be obtained; these curves would resemble normal absorption curves, if the frequency axis were higher. In other words, the plastic behaves as if the loss factor could be broken up into two terms

$$\epsilon'' = \epsilon_s'' + \epsilon''(f) \qquad (4)$$

where ϵ_s'' is the power absorption due to irreversible slipping of molecules in the field against a static friction, and $\epsilon''(f)$ is a frequency-sensitive absorption which reduces to zero in a normal way for both very high and very low frequencies.

As a function of composition at fixed frequency, very interesting curves are obtained. These are shown in Figs. 6 and 7. As plasticizer content increases, the flexibility (plasticity, viscosity) increases, and has its most obvious change in the region centering around 30% plasticizer, where the transition from brittle to soft takes place. In the same range of composition, the dielectric constant has its maximum rate of change, and the loss factor goes through a sharp maximum. This region corresponds to a dispersion which is produced by varying the time of relaxation through

change of internal viscosity, as contrasted to the usual dispersion curves which are obtained by varying frequency at fixed temperature or *vice versa*. A rough estimate of the viscosity of the 60 polyvinyl chloride–40 tricresyl phosphate from the dispersion gives 10^6 poises, which is a reasonable order of magnitude.

The rapid change of viscosity is best illustrated by the change of d. c. conductance with composition, as is shown in Fig. 8. All the samples had as nearly as possible the same thermal history; consequently the hydrogen chloride concentration should be of about the same order in each, and any gross change of κ_0 with composition can be ascribed to changing viscosity. As seen in the figure, the conductance increases exponentially with increasing plasticizer content in the middle of the concentration range.
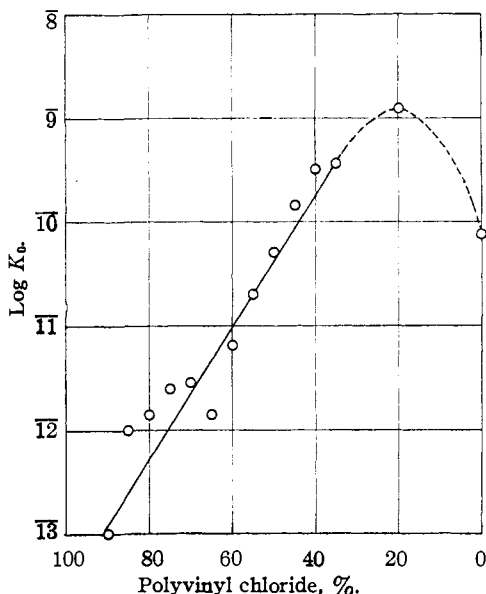

Fig. 8.—Variation of d. c. conductances with composition.

The two ends of the curves of Figs. 6 and 7 exhibit several striking characteristics. The dielectric constant of polyvinyl chloride is at first decreased by the addition of tricresyl phosphate. The decrease is greater than simple volume replacement of relatively more polarizable halogen compound by a compound containing only carbon, hydrogen, oxygen and phosphorus atoms. The index of refraction of tricresyl phosphate at 40° is 1.5494, which gives a specific refractivity.

$$r = (n^2 - 1)/\rho \qquad (5)$$

equal to 1.210; for polyvinyl chloride, $n = 1.565$

and $r = 1.023$. As a function of composition, the electrical susceptibility

$$\sigma = (\epsilon' - 1)/\rho \qquad (6)$$

shows a minimum; and even after subtracting $(p_1r_1 + p_2r_2)$ to allow for the greater polarizability of chlorine atoms, the non-optical susceptibility

$$\sigma^* = (\epsilon' - 1)/\rho - (p_1r_1 + p_2r_2) \qquad (7)$$

still shows a minimum. This may indicate a coupling between the dipoles of polymer and plasticizer.

After this initial decrease in dielectric constant, a minimum appears, followed by the rapid rise already discussed. The maximum which next appears is described most easily as a viscosity effect: starting with pure tricresyl phosphate, we obtain an increase in dielectric constant because we are increasing the content of polar solute, but simultaneously the viscosity increases, so that the two competing influences finally produce a maximum. It is impossible, of course, to consider the properties on a mole fraction scale, because the molecular weight of the polymer is unknown, but we can plot the results on a mole ratio scale, which is proportional to the mole fraction scale. If the susceptibility of the polyvinyl chloride in the plastic, defined by the equation

$$\sigma_1 = (\sigma - p_2\sigma_2)/p_1 \qquad (8)$$

where σ_2 is the total susceptibility of the pure plasticizer, is plotted against the mole ratio, approximate linearity is obtained in the range 0–70% polymer (Fig. 9). The quantity σ_1 extrapolates to 14.5 cc./g. at zero concentration. In order of magnitude, this is a very reasonable figure, if the electrical behavior of the plastic were primarily due to chlorine dipoles in a viscous medium. If we assume that E/F, the ratio of external and in-
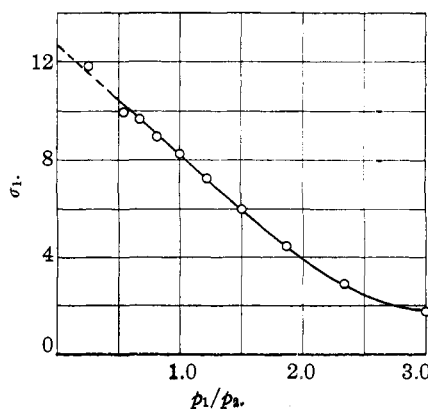

Fig. 9.—Extrapolation of susceptibility.

ternal fields, is of order unity, the molecular polarization per —CH$_2$CHCl— group is 30 cc., because

$$p = \frac{E}{F} \frac{\epsilon' - 1}{3} \qquad (9)$$

This corresponds to a moment equal to 1.2 × 10^{-18}, which compares favorably with the values found for Cl-dipoles in simple molecules, where liquid friction is the only restraint on molecular rotation.
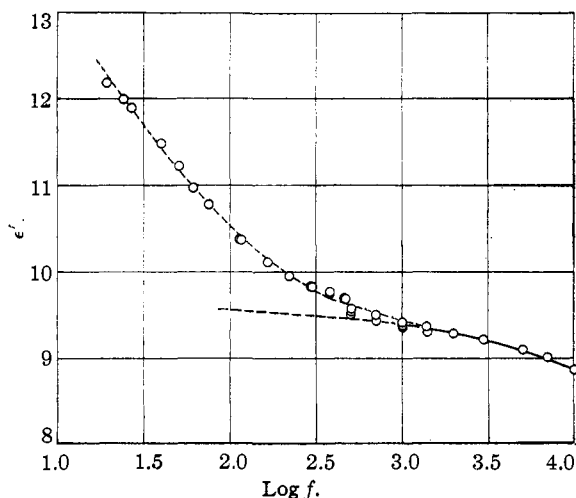

Fig. 10.—Polarization capacitance.

Two other interesting facts are contained in the data. The first is the sudden increase (Fig. 10) with decreasing frequency of the dielectric con-

stant of the 35 polyvinyl chloride–65 tricresyl phosphate sample. This may be due to polarization capacity acting at the electrodes; more data are needed to decide the question. The second is the corresponding rise in loss factor for this sample. If these two properties really are volume properties and not surface effects, the system polyvinyl chloride–tricresyl phosphate has two dispersion regions. The region from the gel stage through the viscous solutions to dilute solutions of polymers in plasticizer needs considerable more investigation, which must be prefaced by a study of experimental methods for handling these materials.

Summary

1. Dielectric constants and loss factors at 40° and 20 cycles to 10 kilocycles under low voltage are reported for the system polyvinyl chloride–tricresyl phosphate, over the entire concentration range.

2. As a function of composition, the maximum absorption and the dielectric dispersion appear in the range 70–50% polymer, where the macroscopic viscosity has its most rapid rate of change with composition.

3. A characteristic difference between free dipoles and dipolar polymers is pointed out: the former can assume a normal distribution of orientations, while the latter have a distribution determined by the chain orientation.
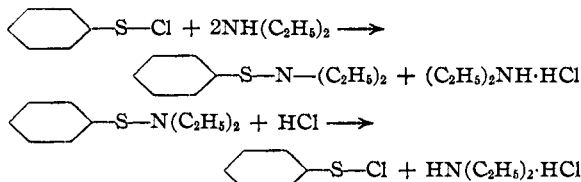

The Use of o-Nitrobenzenesulfenyl Chloride in the Identification of Amines

BY JOHN H. BILLMAN AND EUGENE O'MAHONY

It has been reported by Zincke[1] and Lecher[2] that amines would react with aromatic sulfenyl chlorides to produce amides of sulfenic acid which upon treatment with hydrochloric acid could be hydrolyzed. In certain cases, solid amides were obtained.

The purpose of our work was to investigate further these reactions using substituted benzenesulfenyl chlorides in an attempt to produce suitable solid derivatives of amines for means of identification and to examine the ease of hydrolysis of the amides back to the amines.

It was found that o-nitrobenzenesulfenyl chloride was quite satisfactory as a reagent. The compound is easily prepared and does not react readily with water or alcohol, thereby affording the identification of amines in water solution.

The reactions between reagent and amines were carried out in ether solution and in all cases took place spontaneously. However, no reaction could

(1) T. Zincke and F. Farr, Ann., 391, 57–88 (1912).
(2) H. Lecher and F. Holschneider, Ber., 57, 755–758 (1924).