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Electrical Properties of Solids. XII. Plasticized Polyvinyl Chloride¹

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Introduction

Most linear polymers of high molecular weight are hard brittle solids at room temperatures. On heating, they soften and gradually become more and more flexible and plastic. This property is, of course, the one which makes them useful for molding and extrusion. The flexibility at room temperatures can be increased by the addition of materials of relatively low molecular weight, called plasticizers. With increasing amount of plasticizer, a given polymer becomes softer and more flexible and elastic, going through a rubber-like stage. As more and more plasticizer is added, the material becomes weaker mechanically, soft gel-like substances being produced, and finally (assuming complete miscibility), viscous liquids are obtained. The plasticization of a polymer by a given compound is as specific as solubility relationships among compounds in the ordinary range of molecular weights; as a matter of fact, the two processes of solution and plasticization have many other points of similarity.

In covering the whole range of compositions in the system polymer-plasticizer, many decades of viscosity are spanned, going all the way from the enormous viscosities characteristic of glasses to the relatively low ones of liquids. If polar constituents are present in the plasticized system, we are provided with a tool for investigating the internal dynamics of the system, through its response to an electrical field of variable frequency. Eventually a correlation should be found between the internal dynamics measured through molecular response and the bulk mechanical properties such as elasticity, plasticity, tensile strength and the like.

A knowledge of the generalized dielectric constant

$$\epsilon = \epsilon' - i\epsilon'' \quad (1)$$

where ϵ' is the dielectric constant and ϵ'' the loss factor, furnishes a complete description of the electrical properties of a system. Considered as a vector, ϵ has two components, ϵ' which is 90° out of phase with the field, and measures the capacity of a unit cube, and ϵ'' which is in-phase with the field, and measures the energy dissipated as heat

per cycle in a unit cube. For the 2-component polymer-plasticizer system, we may write

$$\epsilon = \epsilon(f, T, c; a_1, \dots, a_n; b_1, \dots, b_n) \quad (2)$$

where f is the frequency of the applied field, T the temperature, c the composition, and the a_i 's and the b_i 's are molecular parameters characteristic of polymer and plasticizer. In previous papers of this series, we have presented the results of systematic investigations of the dependence of ϵ on frequency²⁻⁷ and temperature³⁻⁶ for several systems, and a few data on variable composition^{2,3,4,7} have been given.

It is the purpose of this paper to present the results of an investigation in which polyvinyl chloride was plasticized with a fairly wide variety of compounds: that is, we are primarily interested here in the variables c and b_1, \dots, b_n of Eq. (2). Measurements were made at 40 and 60° and at 60, 600 and 6000 cycles, over the concentration range 8-30 weight per cent. plasticizer. The measuring temperatures were kept fairly low in order to minimize the uncertain corrections due to direct current conductance.

In the pure polymers, at ordinary temperatures, probably crystallized regions⁸ and amorphous regions are both present. On account of the high viscosity, the time of mechanical relaxation is very great, and hardly any readjustment or further crystallization in quenched polymers is possible. At low or room temperatures, the electrical response of linear polymers like polyvinyl chloride, acetate and chloroacetate¹ is very similar to that reported⁹ for crystallized polyesters. As the temperature is lowered, the similarity of the audio-frequency properties of the linear polymers discussed here to the high frequency properties of the crystalline polyesters becomes steadily more marked. In the pure polymers or in those containing only a small amount of plasticizer, the

(2) Fuoss, *ibid.*, **61**, 3257 (1939).(3) Fuoss, *ibid.*, **63**, 369 (1941).(4) Fuoss, *ibid.*, **63**, 378 (1941).(5) Fuoss and Kirkwood, *ibid.*, **63**, 385 (1941).(6) Fuoss, *ibid.*, **63**, 2401 (1941).(7) Fuoss, *ibid.*, **63**, 2410 (1941).(8) Mark, *J. Phys. Chem.*, **44**, 764 (1940); Bekkedahl and Wood, *J. Chem. Phys.*, **9**, 193 (1941).

(9) Yager and Baker, "Symposium on Electrical Insulation Materials," Atlantic City meeting of the American Chemical Society, Sept. 11, 1941.

(1) Paper XI, *THIS JOURNAL*, **63**, 2832 (1941).

individual dipoles are not free to move, and the broad low absorption band is probably due to the electrical response of the crystallites. As the temperature is raised, or as the plasticizer content is increased, the crystalline regions disappear (melt or dissolve) and with increasing internal mobility, the relatively sharp high peak in absorption characteristic of the dipoles on the polymeric chain appears. With further increase of plasticizer, the dipole maximum shifts to higher frequencies, corresponding to the decreased time of relaxation of the polar groups. These considerations dictated the choice of our concentration range; less than about 8% plasticizer gives plastics which at convenient working temperatures are largely mixtures of amorphous and polycrystalline phases; and at more than about 30% plasticizer, the dipole peak in which we are at present particularly interested, has shifted beyond our working frequency range (60 cycles to 10 kilocycles).

Experimental Details

The *polyvinyl chloride* was a sample from which the low molecular weight components were extracted with warm acetone, by the same procedure which was used to prepare sample A5 for some of the earlier work.^{6,7} Based on its intrinsic viscosity, the weight-average molecular weight is about 98,000.¹⁰

Some of the compounds used for plasticizers were redistilled under low pressure or recrystallized, but most of them were as-received good grade c. p. chemicals. As the work presented below will bear out, the electrical properties of plastics are not very sensitive to small quantities of impurities (other than electrolytic, of course) in the plasticizer.

The plasticizers were dissolved in petroleum ether or in diethyl ether, and added to the polymer. (It was rather interesting to note that diethyl ether swells polyvinyl chloride, while petroleum ether merely wets it.) After stirring until nearly all the solvent had evaporated, the drying was completed in a vacuum oven at 60–100°, depending on the vapor pressure of the plasticizer. Then the powders were placed in a mold at 120°, and after standing closed for two minutes under contact pressure to heat the compound, full pressure was applied for three minutes, after which the mold was cooled (two to three minutes) to room temperature. For the harder samples, 6000 lb./sq. in. were used; this was decreased to 3000 as the plasticizer content in a series increased. The disks were 5 cm. in diameter and 2–3 mm. thick. Measurements at 40 and 60° were made at 60 and 600 cycles, using the Schering bridge and at 6 kilocycles using the parallel bridge. Cells and other details of technique already have been described in previous papers of this series.

The densities of the samples were determined by weighing under water before the aquadag electrodes were

painted on. (The temperatures of the density determinations ranged from 25 to 28°; the appropriate water value was always used, of course. No correction was made to the density of the plastics, however, because they have fairly small expansion coefficients in this range of temperatures: for example, for polyvinyl chloride, $\alpha(30^\circ) = 0.7133$ and $\alpha(50^\circ) = 0.7155$.) The cell constants were then calculated from the weight, density and diameter of the disks. The 40° data were first obtained, and then the 60°; since only four measurements (3 a.c. and 1 d.c.) were made, the samples were in the baths only a short time (approximately thirty minutes) and warping and distortion of the sample was practically negligible.

In order to make uncertainties due to the d.c. conductance as small as possible, 0.5% lead oxide by weight was added in each sample. This amount was sufficient to combine with the hydrogen chloride released by pyrolysis during the pressing, and except in a few cases where the plasticizer contained some electrolytic impurity, the d.c. conductances at 60° were of the order of 10^{-11} to 10^{-12} . The observed d.c. conductance κ_0 in mhos was calculated to an equivalent loss factor ϵ''_0 for each frequency f by the relationship

$$\epsilon''_0 = 9 \times 10^{11} \kappa_0 / 5f \quad (3)$$

For example, a d.c. conductance of 10^{-11} gives a correction $\epsilon''_0 = 0.3$ at 60 cycles, 0.03 at 600 and 0.003 at 6000. This quantity was subtracted from the total observed a.c. loss factor in order to obtain the loss factor ϵ'' for the purely a.c. response.

The densities were corrected for the lead oxide present, but the effect of the lead compounds on a.c. properties will be neglected, because they amount to only 0.06% by volume.

After the electrical measurements were completed, three samples from each series were analyzed for total solids. For the non-volatile plasticizers, the composition determined by analysis always checked that determined by initial weights of polymer and plasticizer; in a few cases, however, some plasticizer was lost during the vacuum drying, and then the analysis gave the composition of the compound actually measured. From the three analyses, a density-composition plot was constructed, and then compositions of the other samples in a given plasticizer series were determined by interpolation.

For analysis, about 2-gram samples were taken from the disks, and cut into pieces a few millimeters square. After weighing to mg., the samples were dissolved in 20 cc. of cyclohexanone by warming on the steam-bath. After diluting to 1% by the addition of 80 cc. of acetone, the polymer was precipitated by carefully adding 200 cc. of methyl alcohol, with constant stirring. After standing overnight to degelatinize, the supernatant liquid (usually perfectly clear and transparent) was decanted through a weighed funnel carrying filter plug of glass cotton in a constriction at the top of the stem. The precipitate (polyvinyl chloride plus lead oxide and chloride) was put to soak several hours more with 100 cc. of fresh methyl alcohol, to complete the degelatinizing, and was then transferred quantitatively to the funnel with the aid of more methyl alcohol. After drying three to four hours in a vacuum oven (0.5 cm.) at 80–85°, the funnels containing the precipitates were weighed, and then as a check were re-

heated and weighed again. Control analyses showed that the procedure was quantitative to 0.1%. The plasticizer content was determined by difference.

Experimental Results

In Fig. 1 are given graphs showing the dependence of specific volume v on composition p for some of the plasticizers studied, where p is weight per cent. of plasticizer in the plastic. (The ordinate scale is displaced vertically 0.01 cc./g. for successive plots; the scale given is for dibenzyl phthalate.). In almost every case, the curve seems to be made up of two straight line segments, with a break around 20% plasticizer. The low concentration segment extrapolates to the volume of unplasticized polyvinyl chloride, while the high concentration one goes to the volume of the plasticizer. The initial slopes, $\Delta v / \Delta p$ are summarized in Table I, along with the values for diphenyl⁴ and tricresyl phosphate.²

TABLE I

INITIAL VOLUME CHANGE ON PLASTICIZATION		
No.	Plasticizer	100 $\Delta v / \Delta p$
1	Dibenzyl phthalate	0.099
2	Dibenzyl maleate	.116
3	Dibenzyl succinate	.125
4	Tricresyl phosphate	.149
5	1-2 Diphenoxyethane	.170
6	Diphenyl	.187
7	Dibenzyl ketone	.188
8	Dibenzyl sebacate	.194
9	Diphenylmethane	.247
10	α -Methylstyrene dimer	.254
11	Dibenzyl	.255
12	Styrene dimer	.264
13	Tetralin	.278
14	Diocetyl phthalate	.282
15	Amylnaphthalene	.283
16	Diphenylmethylmethane	.290

The key numbers in the first column of Table I will be used to refer to the plasticizers in subsequent tables and figures.

If plasticization took place without volume change, the v - p plot would, of course, be a straight line connecting the volumes of the polymer and plasticizer, and $\Delta v / \Delta p$ would numerically equal the difference in specific volumes of the two components. In Table I, it will be seen that a marked contraction appears for the first four esters and also for diphenyl and for dibenzyl ketone. As the polar content of the plasticizer molecule decreases, $\Delta v / \Delta p$ increases, *i. e.*, there is less contraction on mixing. This observation suggests that plasticization depends on an interaction of the fields of the chain dipoles of the polymer and

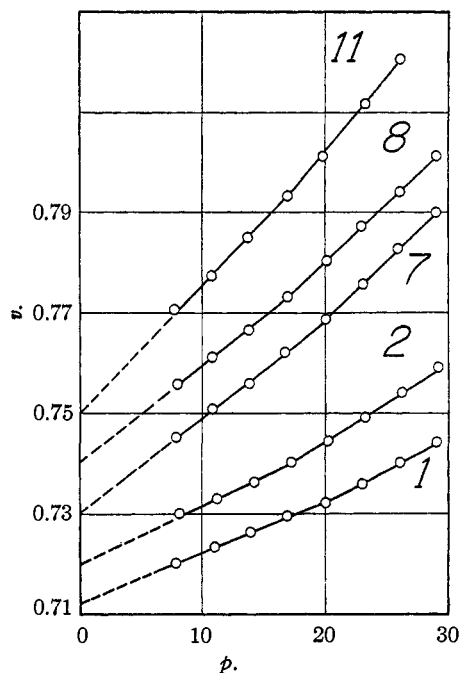


Fig. 1.—Specific volumes as functions of weight percentage for polyvinyl chloride plasticized with dibenzyl phthalate (1), dibenzyl maleate (2), dibenzyl ketone (7), dibenzyl sebacate (8), and dibenzyl (11).

the dipoles of the plasticizer molecule. On this basis, those plasticizers which show the greatest contraction would be most firmly held in the plastic. Qualitative experiments show that the partial pressure of diphenyl in Ph_2 -PVC systems at low concentrations is much less than that calculated by Henry's law, while that of tetralin or amyl naphthalene is not nearly as much reduced. This is, of course, in line with general solution theory; when there are forces between the molecules of the components, the solution is not ideal.

The change in slope around 20% may mean that the internal solution of the plasticizer in the polymer (which locally acts in many ways like a liquid of low molecular weight) becomes saturated at that concentration, and above there, the plastic is something like a two-phase two-component system. For the cases in which the plasticizers were solids at room temperatures, the plastics below the critical concentration were transparent, and above it were opaque-white, although at higher temperatures they again became transparent. The break in the curve may well indicate the saturation concentration; it would be interesting to study these curves as functions of temperature, in order to obtain the solubility coefficient and the heat of plasticization (or solution).

There is a very definite correlation between the structure of a given compound and its ability to plasticize polyvinyl chloride.^{11,12} Broadly speaking, esters, organic phosphates, aromatic hydrocarbons, ketones, ethers and halogenated compounds are plasticizers, provided they do not contain too many aliphatic groups. Aliphatic hydrocarbons, alcohols, phenols, amines, amides, aldehydes, acids and acid anhydrides are in general non-plasticizers; that is, the presence of some polar or polarizable groups is a necessary but not a sufficient condition for plasticization. There are also intermediate cases, such as the benzylic esters of long chain fatty acids (oleates, etc.), which plasticize when hot, but which exude from the plastic on standing at room temperature. Alkyl esters of aliphatic acids are non-plasticizers, while aryl esters of the same acid may plasticize; the plasticizing action can be intensified by making, say, the dibenzyl ester of dibasic acids. A quantitative study of the polymer-plasticizer relationships, along the lines suggested by Brønsted's work¹³ would be a valuable contribution to our knowledge of these systems.

Typical data showing the dependence of electrical properties on concentration for two of the plasticizers studied are given in Tables II and III. In order to save space here, the data for the others have been filed as Document 1602 with the American Documentation Institute.¹⁴

Further examples are given in Figs. 2 and 3. Figure 2 shows dielectric constant (ordinates upper left) and loss factors (ordinates lower right) for dioctyl phthalate as plasticizer at 40° (black points) and 60° (open circles) at 60 and 6000 cycles. This plasticizer gave the lowest and broadest $\epsilon''-p$ curve obtained in this series of compounds; it also gives a very blunt absorption curve with a low maximum on a frequency¹⁴ or temperature¹⁵ scale. Figure 3 gives the same set of curves for diphenylmethane, which gave the sharpest maxima in this series of plasticizers.

Figure 4 gives ϵ' and ϵ'' for the dibenzyl phthalate series at 40 and 60° and 600 cycles; two sets of samples are shown. The first set of disks (open circles) were prepared as described in the previous

(11) M. M. Safori and J. J. Russell, unpublished work in this Laboratory.

(12) J. J. Russell, U. S. Patent 2,227,154, December 31, 1940.

(13) Brønsted, *Comp. rend. trav. Lab. Carlsberg*, **22**, 99 (1937).

(14) For a copy of these data, order Document 1602 from the American Documentation Institute, Offices of Science Service, 2101 Constitution Ave., Washington, D. C., remitting 30 cents for microfilm or 80 cents for photocopies readable without optical aid.

(15) Davis, Miller and Busse, *This Journal*, **63**, 361 (1941).

TABLE II
ELECTRICAL PROPERTIES OF THE SYSTEM POLYVINYL
CHLORIDE-DIPHENYLMETHANE

p	60		600		6000	
	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''
$t = 40^\circ$						
7.31	3.22	0.057	3.15	0.048	3.09	0.060
10.37	3.45	.148	3.28	.105	3.13	.080
13.36	4.13	.454	3.61	.280	3.30	.178
16.42	5.61	.880	4.46	.626	3.64	.408
19.76	6.93	.841	5.58	.857	4.34	.654
22.66	7.65	.633	6.49	.854	5.03	.830
25.76	7.73	.456	6.88	.697	5.56	.835
28.82	7.76	.303	7.19	.497	6.16	.743
$t = 60^\circ$						
7.31	4.85	0.695	4.05	0.429	3.52	0.258
10.37	7.10	1.124	5.44	0.952	4.20	.610
13.36	8.20	0.795	6.71	1.066	4.95	.926
16.42	8.70	.466	7.78	0.827	6.07	1.069
19.76	8.56	.271	8.02	.533	6.78	0.883
22.66	8.45	.184	8.09	.361	7.22	.682
25.76	8.14	.142	7.88	.264	7.22	.521
28.82	7.87	.115	7.69	.180	7.28	.364

TABLE III
ELECTRICAL PROPERTIES OF THE SYSTEM POLYVINYL
CHLORIDE-DIBENZYL SEBACATE

p	60		600		6000	
	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''
$t = 40^\circ$						
7.91	3.32	0.046	3.25	0.043	3.17	0.051
10.79	3.52	.115	3.38	.088	3.23	.076
13.83	4.06	.305	3.70	.211	3.40	.146
16.90	5.02	.579	4.29	.418	3.73	.279
20.06	6.03	.740	5.00	.611	4.14	.439
22.88	6.97	.736	5.82	.735	4.70	.599
25.96	7.47	.638	6.41	.740	5.25	.703
28.95	7.92	.540	7.00	.676	5.85	.753
$t = 60^\circ$						
7.91	4.47	0.440	3.95	0.290	3.57	0.183
10.79	5.94	.826	4.85	.620	4.03	.410
13.83	7.24	.897	5.87	.866	4.63	.646
16.90	8.19	.747	6.92	.906	5.41	.843
20.06	8.58	.560	7.58	.788	6.11	.899
22.88	8.80	.434	8.04	.640	6.75	.854
25.96	8.75	.351	8.17	.506	7.11	.736
28.95	8.76	.295	8.31	.408	7.43	.626

section. After the measurements on them were completed, the aquadag was scraped off, and the samples were thoroughly milled at 100°, after which they were re-pressed into 2" disks. A second series of measurements (black points) were made on the milled samples. The chief difference is that the milled samples show a somewhat broader and lower absorption curve, and a slightly less steep $\epsilon'-p$ curve; no displacement along the p axis was noted. A possible explanation is that the unmilled polymer contained some clumps of

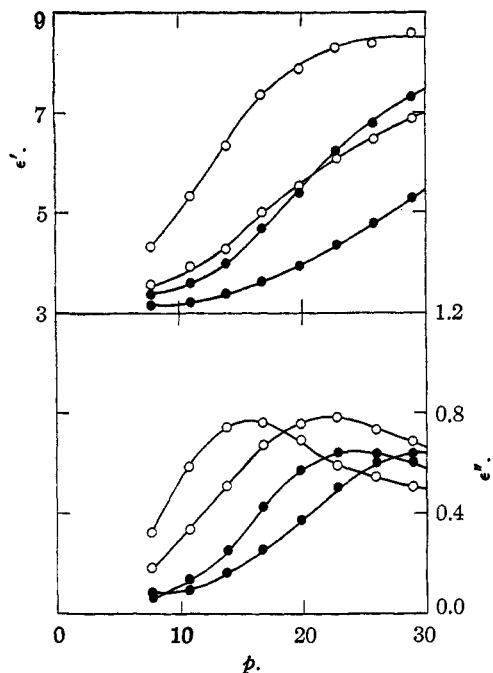


Fig. 2.—Electrical properties of polyvinyl chloride, plasticized with dioctyl phthalate, at 40° (●) and 60° (○), at 60 and 6000 cycles.

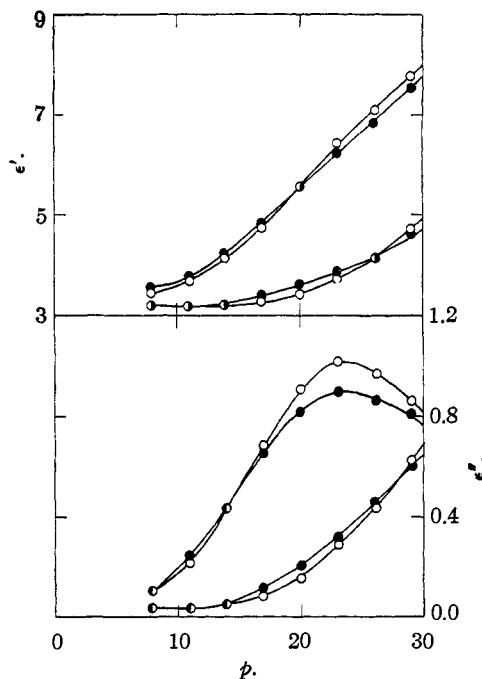


Fig. 4.—Electrical properties at 40° and 60° and 600 cycles of polyvinyl chloride plasticized with dibenzyl phthalate, milled (●) and unmilled (○).

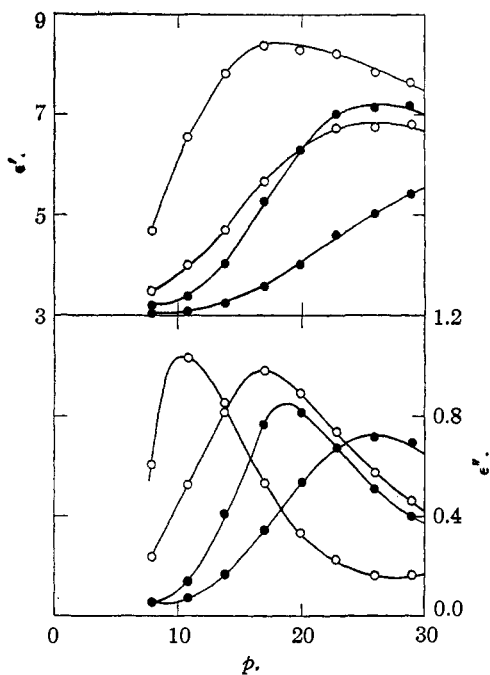


Fig. 3.—Electrical properties of polyvinyl chloride, plasticized with diphenylmethane at 40° (●) and 60° (○), at 60 and 6000 cycles.

tightly interlaced polymer or perhaps some crystalline regions which were smeared out by the milling operation; either effect would broaden the distribution of relaxation times and lower the

maximum in ϵ'' . A similar hint at a slight inhomogeneity in polymers which were not dissolved and reprecipitated was also observed in the viscosity work.¹⁰

Discussion

The general dependence of electrical properties on composition may be inferred from Tables II and III and Figs. 2, 3 and 4. At a given frequency and temperature, say 40° and 600 cycles, the loss factor and dielectric constant are low; with increasing plasticizer content, the loss factor goes through a maximum and the dielectric constant exhibits a sigmoid increase. With further increase of plasticizer, ϵ'' decreases and ϵ' also goes through a maximum if the static constant of the plasticizer is lower than that of polyvinyl chloride. Qualitatively, these effects are quite easy to explain: at low plasticizer content, the internal viscosity η is very high, and in this range of frequency, little individual dipole response appears. With increasing plasticizer concentration, the viscosity decreases, and with it the times of relaxation of the segments of the polar polymer which become increasingly free to follow the field. When the most probable relaxation time¹⁶ (which is proportional to η) reaches the reciprocal of 2π

(16) Kirkwood and Fuoss, *J. Chem. Phys.*, 9, 329 (1941).

times the measuring frequency, the maximum phase difference between the dipole motion and the field is reached, corresponding to a high value of loss factor. With further decrease in viscosity, the dipoles approach motion in phase with the field, corresponding to a decreasing loss factor and an increasing dielectric constant. On further dilution, the loss factor will decrease to zero (unless another absorption band, whose presence is now unsuspected, appears), and the dielectric constant will approach that of the plasticizer. A maximum obviously appears in the $\epsilon''-p$ curve if the plasticizer has a low dielectric constant, as for example appears for the hydrocarbons.

With increased temperature, the loss factor maximum for a given frequency shifts to lower concentrations, because the viscosity decreases both with increased temperature or increased plasticizer content, and hence less plasticizer is needed at a higher temperature to reach a critical relaxation time determined by a fixed measuring frequency. It will also be noted that, at a given temperature, the concentration corresponding to the maximum in the $\epsilon''-p$ plots shifts to lower concentrations with decreasing frequency, because the critical relaxation time increases inversely as the frequency. The data presented here show that the internal viscosity is extremely sensitive to plasticizer concentration: for example, with diphenylmethane, the 60 cycle peak appears at 10.40% and the 6000 cycle peak at 15.85%, both at 60°. In other words, a change of a little over 5% in internal composition produces a hundred-fold change in internal viscosity.

In order to compare the plasticizers of Table I quantitatively, it is necessary to reduce the mass of data to some simple numerical form. Empirically, it is possible to represent the loss factors by an equation of the same form

$$\epsilon''/\epsilon''_{\max.} = 2z/(1 + z^2) \quad (4)$$

as was used in the temperature analysis³; just as in that case, we may *not* identify z with the $\omega\tau$ of Debye's theory, because the polymeric system is characterized by a distribution of relaxation times, rather than by a single relaxation constant. However, we may expect that the changes in z will have a close correspondence to the changes in viscosity, judging from the results obtained at constant composition and variable temperature. It was found that z defined by (4) and the composition are related by the simple empirical formula

$$\log z = \lambda \log p/p_m \quad (5)$$

where p is the number of grams of plasticizer per 100 g. of plastic, p_m is the concentration at which the maximum in the $\epsilon''-p$ curves (e. g., Figs. 2, 3, 4) appears, and λ is a constant for given frequency, temperature and plasticizer. In Tables IV and V are summarized the constants of Eq. (5) for the plasticizers of Table I.

TABLE IV
CONCENTRATIONS FOR LOSS FACTOR MAXIMA

No.	60	40° 600	6000	60	60° 600	6000
1	19.3	23.3	28.5
2	24.7	28.2	33.9	14.8	17.7	22.2
3	22.9	24.8	30.5	14.3	17.2	21.1
5	13.7
7	21.0	23.7	28.5	12.6	14.9	19.3
8	21.5	24.3	29.2	13.4	15.9	19.7
9	17.9	21.2	24.1	10.4	12.5	15.9
10	16.7	18.4	19.1
11	19.3	21.8	25.1	11.2	14.0	17.2
12	18.7	21.5	24.0	10.9	13.2	16.6
13	18.0	20.4	23.4	10.4	12.4	15.5
14	24.8	27.4	32.7	15.7	18.8	22.0
15	22.4	25.4	31.4	13.4	16.3	20.9
16	19.3	21.9	24.8	11.3	13.7	17.2

TABLE V
 λ -VALUES FOR DIFFERENT PLASTICIZERS

No.	60	40° 600	6000	60	60° 600	6000
1	3.00	2.95	2.85
2	3.95	3.65	3.45	2.85	2.70	2.60
3	4.25	4.10	3.45	2.95	2.90	2.70
5	2.65
7	3.95	4.25	3.85	2.80	3.00	2.85
8	3.50	3.45	3.10	2.70	2.50	2.35
9	3.70	3.70	3.60	3.05	3.00	2.85
10	4.50	4.50	..	3.10	3.15	3.35
11	4.10	4.25	3.90	3.25	3.05	2.75
12	3.50	3.40	3.05	2.90	2.75	2.55
13	3.85	3.90	3.75	2.90	2.85	2.85
14	2.45	2.60	2.45	2.15	2.15	2.05
15	3.90	3.65	3.15	3.05	3.00	3.00
16	3.80	3.80	3.55	3.15	2.90	2.80
4	(40° and 1000 ~) = 3.7					

Typical test plots of Eq. 5 are shown in Fig. 5, using dibenzyl as an example, where $\log z$ is plotted against $\log p$. It will be seen that straight lines average the points quite satisfactorily. The value of p_m , the concentration for the maximum, is determined by the intersection of the line with the axis at $\log z = 0$. A few of the figures of Table IV represent extrapolated values. The slopes of the lines of Fig. 5 are measures of the rate of change of viscosity with concentration of plasticizer, the latter reckoned as ratios to the concentration at which the maximum loss appears for a given temperature frequency. These

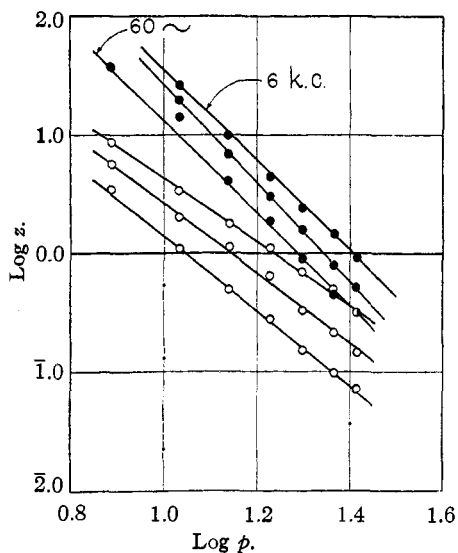


Fig. 5.—Test plot for Eq. (5): dibenzyl data at 40° (●) and 60° (○).

slopes, given in Table V, are roughly independent of frequency, and decrease rapidly with increasing temperature. If dioctyl phthalate (lowest) and α -methylstyrene dimer (highest) are excluded, the slopes are not very sensitive to plasticizer structure, giving about 3.5 to 4 at 40° and 2.5 to 3 at 60°. Assuming that z is a measure of the relaxation time, this means that the viscosity changes very much faster than the concentration, approximately as its third or fourth power. It is expected that the empirical formula will not hold at high plasticizer concentrations (*i. e.*, in the range where it would be more proper to speak of solutions of polymer in the plasticizer than of plasticized polymer) where the dependence of viscosity on concentration will be considerably reduced over that appearing in the hard-to-flexible range considered here. It also should be mentioned that, while the ϵ'' - p plots are unsymmetrical about the maximum, the ϵ'' - $\log p$ plots are symmetrical; that is, the amount of plasticizer calculated with respect to the corresponding p_m is the significant independent variable, rather than the absolute amount.

At first glance, the concentrations for maximum ϵ'' at a given frequency and temperature seem to be quite unsystematic as far as the structure of the plasticizer is concerned. If we consider the different plasticizers in sequence of increasing molecular weight, however, a definite regularity appears. Physically, the p_m value means the concentration of plasticizer necessary to reach a definite internal viscosity which, although still

unknown, is exactly specified by the frequency and temperature. That is, a characteristic electrical response, such as maximum loss factor at fixed frequency and temperature, provides a quantitative basis for comparing the effects of different substances on the internal mechanics of the plastics. If we start with undiluted polymer, we presumably have a close-packed structure which may be almost entirely polycrystalline¹⁷ or, depending on its chemical structure, it may contain crystallized regions separated by amorphous regions in which the chains have random orientation. In any case, there is practically no freedom for motion of chain segments. If we add plasticizer, we are inserting small molecules between chains, and in so doing, break the chain to chain coupling,⁴ either by dilution of the amorphous phase or by solution of the crystalline phase. This leads to two effects: first, the absorption due to the pure polymer structure disappears (the low temperature ϵ'' -maximum) and, second, the internal viscosity decreases, allowing the dipole absorption to begin (the high temperature ϵ'' -maximum). Now the larger the number of small molecules added, the greater will be the number of places where the chain structure is opened up. Consequently we expect and find that a smaller weight per cent. of a low molecular weight plasticizer is needed to give a given electrical response than of a plasticizer of high molecular weight. This is shown graphically in Fig. 6a, where p_m for 60° and 60

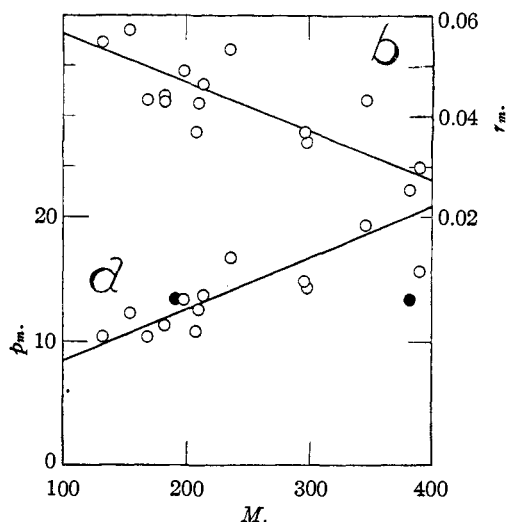


Fig. 6.—Dependence of plasticizing ability on molecular weight M : (a) weight per cent. for 60° - 60° ~ maximum; (b) mole ratio for 60° - 60° ~ maximum.

(17) Mooney, THIS JOURNAL, 63, 2828 (1941).

cycles is plotted against M , the molecular weight of the plasticizer. For example, 10.4% tetralin ($M = 132$) gives the same effective viscosity as 19.3% dibenzyl phthalate ($M = 346$). The points of Fig. 6 scatter quite a bit, of course, because the number of molecules is only one of the variables involved. Two compounds, dibenzyl sebacate and dioctyl phthalate, are markedly different from the average. If the former is plotted at one-half its molecular weight (black points in Fig. 6a), however, it conforms to the general pattern: in other words, one molecule of $C_6H_5CH_2CO_2(CH_2)_8CO_2CH_2C_6H_5$ acts like two independent molecules of plasticizers, on account of the long flexible methylene chain between the two polar (plasticizing) ends. Dioctyl phthalate is, as has been mentioned before, exceptional in many ways, and is very different in structure from the other compounds of Table I.

If we calculate compositions on a mole ratio basis, the regularities discussed above appear very clearly, and further specific differences due to structure appear. If merely number of particles were all that was involved, the mole ratios would be the same for all plasticizers for a given electrical response; if we consider the mechanism of plasticization, however, we see that the shape as well as the size of the plasticizer molecule must also be taken into account. In Table VI, the plasticizers are arranged in sequence of molecular weights, which are given in the second column, and in the third and fourth columns are given r_{60} and r_{6000} , the mole ratios corresponding to the 60° maxima for 60 and 6000 cycles, respectively.¹⁸

TABLE VI
DEPENDENCE OF PROPERTIES ON PLASTICIZER

No.	M	r_{60}	r_{6000}	r_{6000}/r_{60} (25°, 60°)
13	132	0.0546	0.0867	..
6	154	.0579	.0960	..
9	168	.0432	.0699	8.40
16	182	.0440	.0714	8.40
11	182	.0434	.0714	8.30
15	198	.0489	.0833	8.15
12	208	.0368	.0660	8.30
7	210	.0426	.0710	12
5	214	.0462	..	9.5
2	296	.0367	.0594	10.3
3	298	.0349	.0560	10.4
1	346	.0431	.0719	19.0
8	382	.0254	.0399	9.6
14	390	.0298	.0451	..

(18) The mole ratio is defined here as $r = (p/M)(62.5/(1 - p))$; that is, the mole ratio is reckoned in terms of monomoles of polyvinyl chloride ($m = 62.5$) because plasticizer-polymer interaction is local, and only a small part of the polymeric chain is affected by a single plasticizer molecule.

We first note one rough parallelism between r and M : r tends to decrease as M increases (Fig. 6b) or, to put it another way, a given number of large molecules reduces the viscosity more than the same number of smaller molecules. The length of the plasticizer molecule seems to be the significant variable, which is reasonable if the mechanism involved is a separation of chains. For example, diphenylmethane, diphenylethane (1,1 and 1,2), dibenzyl ketone, and diphenoxyethane all have r_{60} values of about 0.04+, and they all are roughly similar from an architectural point of view. The two smaller, more compact molecules diphenyl and tetralin have considerably larger r_{60} values, while the long ester molecules have smaller r_{60} values. If one constructs scale models of these molecules, and measures their average over-all length L , the product Lr is reasonably constant. Consequently, we conclude that the number, shape and size of the plasticizer molecules are the important variables in determining the properties of plasticized polymers.

The great sensitivity of internal friction to plasticizer content is well illustrated by the data of Table VI. The ratio r_{6000}/r_{60} is independent of plasticizer structure, and averages to 1.62. We see that a 62% increase in number of plasticizer molecules, regardless of their structure, decreases the resistance to internal motion by a factor of 100.

A calculation of the dipole moments μ per monomer unit⁵ was made for the hydrocarbon plasticizers. Only three frequencies were available but, even so, fairly accurate values of the static dielectric constants necessary for the calculation could be obtained at 60° by Cole's method¹⁹ of extrapolation using a circular arc. The results of the calculation are summarized in Table VII; they are in excellent agreement with previous^{5,7} values of $\mu(-CH_2CH_2Cl-)$ obtained in the same range of concentration.

No calculations were made on the systems containing polar plasticizers, because not enough is yet known about them. The peak in absorption for the polar plasticizer molecules probably comes at much higher frequencies, because the maximum due to chain dipoles apparently does not depend on whether the plasticizer is polar or hydrocarbon. A theoretical analysis of the results with polar plasticizers must wait until a simpler problem, that of the behavior of small polar molecules in non-polar polymers, has been treated.

(19) Cole and Cole, *J. Chem. Phys.*, **9**, 341 (1941).

TABLE VII
DIPOLE MOMENTS PER MONOMER UNIT

ρ	μ	ρ	μ
Distyrene		1,2-Diphenylethane	
19.9	2.17	19.8	2.16
22.8	2.16	23.2	2.16
25.6	2.16	26.0	2.13
28.6	2.05		
Diphenylmethane		Tetralin	
19.8	2.17	19.3	2.21
22.7	2.16	22.3	2.22
25.8	2.16	25.2	2.20
28.8	2.15	28.3	2.20
1,1-Diphenylethane		Amylnaphthalene	
19.9	2.16	23.0	2.13
22.8	2.16	25.9	2.12
25.9	2.13	29.0	2.11
28.8	2.13		

In order to give some information on the influence of plasticizer on polar properties, in the last column of Table VI are given values of the static dielectric constants at 60° for 25% plasticizer. These are values obtained by interpolation on an ϵ_0 - ρ plot, for which the ϵ_0 values were obtained by the Cole extrapolation. It will be noted that ϵ_0 is larger for the polar plasticizers than for the hydrocarbons, which average to $\epsilon_0 = 8.3$. Diphenoxyethane comes somewhat higher, due to the polarity of the oxygens, and the esters are still higher. Dibenzyl sebacate is low, because the molecule contains a lot of non-polar methylenes, and dibenzyl ketone is highest. A very definite parallelism between the static dielectric constant at a given temperature and composition, and the relative dipole content of the plasticizer molecule is thus observed.

Summary

1. Data at 40 and 60°, at 60, 600 and 6000 cycles are given for polyvinyl chloride plasticized with 8 to 30% by weight of the following compounds: tetralin, diphenylmethane, diphenylmethylmethane, dibenzyl, amylnaphthalene, distyrene, di- α -methylstyrene, diphenoxyethane, dibenzyl ketone, dibenzyl maleate, dibenzyl succinate, dibenzyl phthalate, dibenzyl sebacate and dioctyl phthalate.

2. Plasticization is essentially a separation of chain molecules by the plasticizer molecules, accompanied by a rapid decrease in microscopic and macroscopic coefficients of friction.

3. A simple empirical relationship connecting loss factor and plasticizer concentration is given. Very roughly, the viscosity varies inversely as the third or fourth power of the relative concentration, depending on the temperature.

4. The concentration at which a given plasticizer produces a given internal viscosity, as measured by a characteristic electrical response, depends on the size and shape of the plasticizer molecule. A long cylindrical molecule is more effective in reducing viscosity than a spherical molecule of the same molecular weight.

5. Plasticizers of about the same size and shape are about equally effective as plasticizers, regardless of their chemical structure. For polyvinyl chloride, however, a polar or polarizable group must be present in the plasticizer in order for it to interact with the polymer.

SCHENECTADY, N. Y. RECEIVED NOVEMBER 8, 1941

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, NEW YORK STATE COLLEGE FOR TEACHERS, AND COLUMBIA UNIVERSITY]

A Study of the Reaction of Ferric Ion with Orthophosphate in Acid Solution with Thiocyanate as an Indicator for Ferric Ions

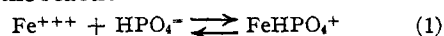
BY OSCAR E. LANFORD AND SAMUEL J. KIEHL

Introduction

It is well known that the addition of orthophosphoric acid to an acid solution of a ferric salt produces an extensive decrease in the activity of the ferric ions. This property probably constitutes the fundamental principle in the effectiveness of the Zimmerman-Reinhardt "Preventive Solution."^{1,2} Beyond this, however, little is known

concerning the reaction of ferric ions with phosphate. Therefore, to ascertain its nature and to discover, if possible, the type and formula of the complex formed, the present investigation was undertaken.

By the method used we were able not only to establish the reaction



but also to determine the dissociation constant of FeHPO_4^+ , the ferric phosphate complex formed. The method suggested by the recent

(1) Zimmerman and Reinhardt, *Ber.*, **14**, 775 (1881); *Chem. Ztg.*, **13**, 323 (1889).

(2) H. A. Fales and F. Kenny, "Inorganic Quantitative Analysis," The Century Company, New York, N. Y., 1939, p. 426.