

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

Electrical Properties of Solids. X. The System Polyvinyl Chloride-Tetrahydronaphthalene

BY RAYMOND M. FUOSS

I. Introduction.—Methods have been presented in previous papers of this series which permit the determination of the dipole moment $\tilde{\mu}$ per monomer unit¹ from measurements on absorption and dispersion in the audiofrequency range on solids containing polar polymers. The moment so obtained is independent of the degree of polymerization² and becomes independent of temperature³ above the transition temperature of the plastic. For a linear polymer of the type $(\text{CH}_2\text{CHCl})_n$, in dilute solution in a non-polar solvent, $\tilde{\mu}$ has the calculated value $\sqrt{3}\mu_0/2$, where μ_0 is the moment of the polar group in free space. Experimental data for the system PVCl-Ph₂ gave moments of the correct order of magnitude, but showed a rather marked concentration dependence, especially in the more concentrated region. The range 0–20% diphenyl was covered in the earlier work, and could not be extended conveniently because the diphenyl crystallized out on cooling for concentrations greater than 20%. With tetrahydronaphthalene ("tetralin"), this range can be doubled. Results presented in this paper show that the moment per monomer unit approaches the required theoretical limit as dilution increases.

The increase of $\tilde{\mu}$ with decreasing temperature or increasing polymer content can be explained in terms of hindered rotation. In calculating the average moment

$$\mu = \mu_0 \sqrt{3}/2 \quad (1)$$

free rotation at each C–C bond was assumed for simplicity and, in averaging, many configurations which involved an (impossible) interpenetration of the chain were included. Dipole-dipole interaction along the chain or with neighboring chains was also neglected. All these effects lead to a less curled up structure for the polymer, and it will be shown that extension of the chain increases the average moment.

II. Materials and Procedure.—The polyvinyl chloride was the A5 sample described in the previous paper.² Briefly, it was a polymer from

which the low molecular weight material had been extracted by warm acetone. Eastman Kodak Co. practical tetralin was distilled; the middle fraction, boiling at 90° and 25 mm., was used as the hydrocarbon plasticizer.

The tetralin was diluted with petroleum ether (b. p. $\leq 50^\circ$), and added to a weighed amount of polymer. After stirring thoroughly, the ether was evaporated in a vacuum oven at 50°. Disks for electrical measurements were pressed at 120°. Care was taken to lose no solids, and the tetralin concentration was calculated from the final weight of the disk and the initial weight of polymer. The samples with higher concentrations of tetralin gradually lost plasticizer by evaporation, but by placing the disk in the cell immediately after weighing it and measuring its thickness, this loss was kept negligible.

Densities were determined from the dimensions of the samples and their weights. Specific volumes are given by the following equation which averages these data

$$v = 0.710 + 0.00325p \quad (2)$$

where p is the weight percentage of tetralin ($V = 1.03$). Equivalent air capacities were calculated from the density, weight and diameter of the disks.

III. Experimental Results.—Dielectric constants and loss factors at 60 cycles to 10 kilocycles at a variety of temperatures are given in Table I for the five concentrations investigated. The temperatures were chosen to bring the peak loss factor into the working frequency range for each of the plastics. In general, the viscosity at a given temperature decreases with increasing plasticizer content, and for a fixed composition decreases with increasing temperature, so with increasing tetralin content, the working temperature range was lowered. The d. c. conductances, given in the lower section of Table I, were measured, and subtracted⁴ from the total a. c. conductances before computing ϵ'' , the loss factor.

The frequencies for the maxima were obtained by plotting $\cosh^{-1}(\epsilon''_m/\epsilon'')$ against $\log f$, and noting the intersection of the curves with the hori-

(1) Fuoss and Kirkwood, *THIS JOURNAL*, **63**, 385 (1941).

(2) IX, Fuoss, *ibid.*, **63**, 2401 (1941).

(3) Fuoss, *ibid.*, **63**, 378 (1941).

(4) For a discussion of this correction, see Fuoss, *THIS JOURNAL*, **63**, 369 (1941).

TABLE I
ELECTRICAL PROPERTIES OF POLYVINYL CHLORIDE-TETRALIN SYSTEMS

	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''	ϵ'	ϵ''
8.3% C ₁₀ H ₁₂								
	$t = 75^\circ$		$t = 80^\circ$		$t = 55^\circ$		$t = 60^\circ$	
60	8.21	0.859	8.96	0.681	7.94	0.547	8.26	0.441
120	7.81	.932	8.64	.776	7.68	.619	8.07	.493
240	7.37	.975	8.27	.870	7.39	.689	7.84	.565
480	6.89	1.009	7.85	.956	7.05	.756	7.57	.645
1 kc	6.38	1.005	7.33	1.013	6.64	.816	7.21	.724
2	5.88	0.977	6.79	1.057	6.21	.865	6.83	.803
3	5.60	.947	6.48	1.064	5.96	.877	6.59	.847
6	5.11	.876	5.88	1.041	5.43	.872	6.09	.893
10	4.73	.800	5.39	0.987	4.98	.836	5.60	.898
25.9% C ₁₀ H ₁₂								
	$t = 20^\circ$		$t = 25^\circ$		$t = 30^\circ$		$t = 35^\circ$	
60	6.02	0.548	6.50	0.519	6.90	0.462	7.17	0.394
120	5.77	.563	6.26	.548	6.69	.496	7.00	.427
240	5.51	.575	6.01	.580	6.46	.539	6.81	.470
480	5.25	.575	5.74	.598	6.21	.576	6.59	.519
1 kc	4.99	.565	5.45	.604	5.93	.609	6.32	.567
2	4.73	.552	5.16	.613	5.63	.635	6.04	.614
3	4.55	.534	4.97	.606	5.43	.647	5.84	.637
6	4.24	.501	4.61	.585	5.08	.645	5.49	.664
10	4.06	.467	4.36	.556	4.74	.625	5.13	.661
25.9% C ₁₀ H ₁₂								
	$t = 40^\circ$		$t = 15^\circ$		$t = 20^\circ$		$t = 25^\circ$	
60	7.31	0.359	6.14	0.504	6.55	0.475	6.85	0.425
120	7.17	.370	5.91	.519	6.34	.501	6.67	.452
240	7.02	.401	5.67	.536	6.10	.531	6.46	.484
480	6.84	.453	5.42	.544	5.86	.553	6.24	.524
1 kc	6.62	.505	5.17	.542	5.58	.572	5.98	.554
2	6.38	.564	4.92	.535	5.31	.581	5.70	.586
3	6.21	.595	4.74	.529	5.14	.583	5.52	.599
6	5.87	.645	4.44	.504	4.78	.571	5.20	.607
10	5.63	.661	4.24	.476	4.52	.550	4.87	.596
39.1% C ₁₀ H ₁₂								
	$t = 5^\circ$		$t = 10^\circ$		$t = 15^\circ$		$t = 20^\circ$	
60	5.54	0.385	5.88	0.372	6.06	0.337	6.32	0.303
120	5.36	.395	5.71	.386	5.91	.352	6.20	.315
240	5.18	.403	5.54	.403	5.75	.371	6.06	.337
480	5.00	.411	5.35	.420	5.58	.396	5.90	.366
1 kc	4.81	.413	5.15	.432	5.43	.418	5.75	.391
2	4.60	.411	4.93	.438	5.20	.439	5.54	.428
3	4.49	.409	4.81	.443	5.05	.450	5.42	.443
6	4.26	.400	4.54	.442	4.81	.462	5.16	.471
10	4.05	.388	4.36	.426	4.62	.454	4.94	.480
8.3%								
t	$10^{10} \kappa_0$	$\log f_m$	β					
75°	0.002	2.85	0.328					
80°	.006	3.42	.370					
17.1%								
55	0.008	3.58	0.361					
60	.014	3.94	.411					
25.9%								
20	0.003	2.58	0.249					
25	.007	3.11	.286					
30	.014	3.70	.287					
35	.025	(4.06)	.320					
40	.042	(4.38)	.347					
32.6%								
t	$10^{10} \kappa_0$	$\log f_m$	β					
15	0.004	2.88	0.227					
20	.008	3.37	.273					
25	.014	3.69	.334					
39.1%								
5	0.007	3.00	0.193					
10	.011	3.40	.218					
15	.021	3.80	.305					
20	.037	(4.20)	.331					
25	.061					

zontal axis. The lower concentrations gave linear plots, but the 32.6 and the 39.1% samples gave curves which were concave down. As seen in Fig. 1, $\log f_m$ is linear in $1/T$; for comparison, the d. c. conductance (points solid black) for one of the samples (25.9%) is also plotted on the same figure. The resistance to dipole rotation has a somewhat larger temperature coefficient than the resistance to ionic migration, but both are of the order of 40 kcal.

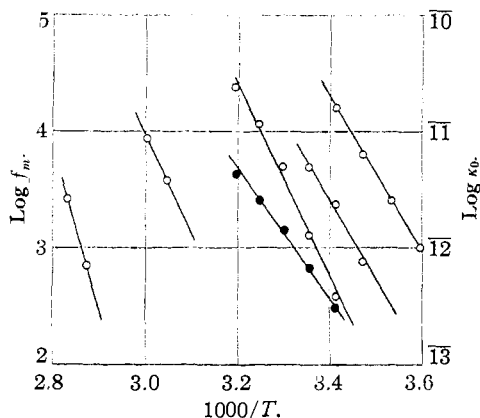


Fig. 1.—Dependence of relaxation on temperature.

IV. Discussion.—The moments were calculated from the data by the method developed in the previous paper, using Cole's arc function⁵ to extrapolate for ϵ_0 , the static dielectric constant, after determining β , the distribution parameter, from the maximum loss factor and a value one decade away from the maximum. As in the diphenyl case, the values of $\tilde{\mu}$ approached values independent of temperature as the temperature increased. The asymptotic values obtained are plotted against per cent. plasticizer in Fig. 2, together with the previous values obtained for the diphenyl system (solid black points). The moment of a number of simple molecules like methyl chloride, ethyl chloride, etc.,⁶ gives $\mu_0 = 2.00$ Debye units. Substituting in (1), we find $\tilde{\mu} = 1.73$ as the expected value for the Cl-dipoles in polyvinyl chloride. Figure 2 shows that the experimental values are approaching this as the limit as dilution increases.

The positive deviations may be understood qualitatively by considering an improbable configuration, that of the extended chain. This is defined as the configuration in which the distance

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

(6) Smyth, "Dielectric Constant and Molecular Structure," A. C. S. Monograph, Reinhold Publ. Corp., New York, N. Y., 1930.

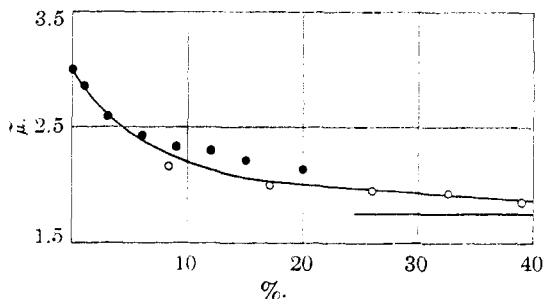


Fig. 2.—Variation of moment $\tilde{\mu}$ with hydrocarbon content of plastics.

between the terminal carbon atoms has its maximum value. There are 2^n extended configurations which are obtained by distribution of the n chlorine atoms among the *cis*- and *trans*-positions in the n monomeric units of the chain, if we assume a head-to-tail structure for the polymer and free rotation at each C-C bond. For any pair of monomers, say the k -th and l -th, we have for the cosine of the angle γ_{kl} between the dipoles

$$\cos \gamma_{kl} = (\cos \gamma_{cc} + \cos \gamma_{ll} + \cos \gamma_{cl} + \cos \gamma_{lc})/4$$

where $\cos \gamma_{cc}$ or $\cos \gamma_{ll}$ is unity, and the cosine for the *cis-trans* positions is $(-1/3)$. Averaging, we have

$$\overline{\cos \gamma_{kl}} = 1/3 \quad (3)$$

There are $n(n-1)$ such terms with $k \neq l$ in the sum S_n which is used to compute the mean square moment.⁷ We therefore obtain for the extended chain a total moment M given by

$$M^2 = n(n+2)\mu_0^2/3 \quad (4)$$

The mean moment per monomer unit is $\sqrt{M^2/n}$, which gives

$$\mu_{ex} = \mu_0 \sqrt{(n+2)/3} \approx \mu_0 \sqrt{n/3} \quad (5)$$

This is, of course, an enormous value, and is caused by the probability of parallel components increasing with \sqrt{n} in the extended chain. As stated before, this configuration has a low probability of occurrence; the value of the calculation lies in the fact that it shows that any influence which prevents curling up of the chains (attainment of maximum entropy) simultaneously acts to increase the average moment.

Summary

1. Absorption and dispersion measurements in the range 60 cycles to 10 kilocycles are reported for the system polyvinyl chloride-tetrahydronaphthalene at temperatures which bring the maximum absorption into the frequency range

(7) Equations 65-68 of ref. 1.

given. Plastics containing up to 40% hydrocarbon by weight are covered.

2. The mean moment per (CH₂CHCl) group is shown to approach 1.73 *D* with increasing dilution, which is the theoretical limit for a linear polar polymer of alternating structure, assuming

free rotation. Positive deviations at high concentrations of polymer or low temperatures are explained qualitatively as an increase of average moment due to configurations in which the chain molecules are not in their most probable state.

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The Heat Capacity of Gaseous Paraffin Hydrocarbons, Including Experimental Values for *n*-Pentane and 2,2-Dimethylbutane

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Although several accurate experimental entropies are now available for the paraffin series, the gaseous heat capacity data are sparse and mostly of doubtful accuracy. Several years ago the writer started work on gaseous specific heat measurements by the flow method, which seemed the most direct among those capable of giving reasonable accuracy and which has given some of the best results in the past. It was decided at the beginning that the calorimeter was to be designed for substances boiling above room temperature, and that the results must be absolute and not merely relative to some one compound. Some preliminary results already have been published,¹ and the work presented below tends to confirm their correctness.

The general method used by Bennewitz and Rossner² was adopted but with complete change of detailed design. As is shown in Fig. 1, this general method consists of establishing the flow of vapor by electrical evaporation of the liquid at a constant rate. In our final apparatus a continuous cycle is employed, the condensed vapor being returned to the vaporizer chamber as liquid at the boiling point. Suffice it to say here that the accuracy of the resulting heat capacities appears to range from about 0.3% near room temperature to about 1% at 200°C. Heats of vaporization reliable to about 0.3% are also obtained.

In the discussion of the results in terms of statistical calculations, it is shown that the barriers to internal rotation in *n*-butane and pentane are probably about 3600 cal. per mole instead of the 30,000 and 16,000 cal. values which also have been proposed.

(1) K. S. Pitzer, *THIS JOURNAL*, **62**, 1224 (1940).

(2) K. Bennewitz and W. Rossner, *Z. physik. Chem.*, **B39**, 126 (1938).

Design and Operation of Apparatus

The essentials of a good flow calorimeter include (1) a constant, accurately measured rate of flow, (2) a heater to introduce an accurately measured amount of heat into the gas, (3) thermometers that measure the temperature of the gas itself, and (4) a design which prevents excessive heat loss between heater and thermometer and which permits accurate correction for the loss occurring.

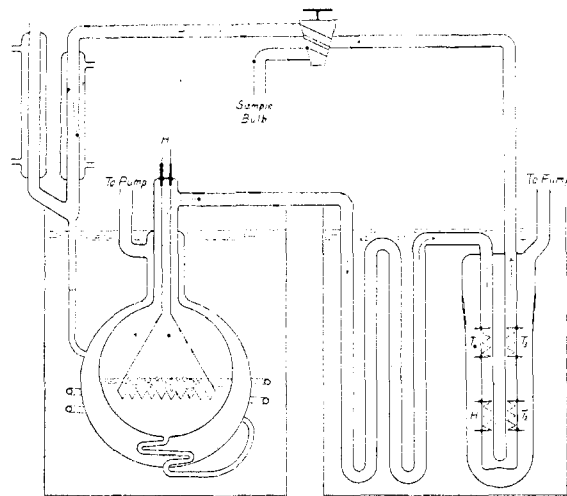


Fig. 1.—Diagram of the apparatus. Certain parts are omitted for simplicity.

A diagram of the calorimeter is shown in Fig. 1. The gas flow was produced by electrically evaporating the liquid at a constant, accurately measured rate. A spherical, double-walled glass vessel was constructed from 1- and 2-liter flasks, which had a long straight double-walled neck at the top. At the bottom a small tube spirals from the inner container to the outside. The heater is a large double spiral of no. 22 chromel wire (11 ohms) mounted somewhat below the center of the inner vessel. Preliminary experiments showed that at least 300 watts could be introduced with this heater into typical organic liquids without excessive wire temperatures. In operation the liquid level is 1 to 2 cm. above the heater wire. The liquid boils smoothly around the heater, the flow being satisfactorily