

If two or more HJ straight lines are observed for a single isotherm the ratios of the square roots of their slopes allows identification of the type of film obtained and the proper constant may then be selected. If only one straight line is observed identification of the film is impossible without further information. This information may be (a) the absolute area of the solid or (b) the BET area value. The first alternative is of course not available in routine measurements of surface area. The type of film must then be identified by selecting that constant which yields an area in best agreement with the BET value. Under these circumstances the HJ area serves to confirm that obtained by the BET calculation.

Forty isotherms were measured in this investigation. In ten isotherms two or more unquestionable straight lines were obtained in the HJ plot; it was possible in these instances to select the proper HJ constant independently of the BET calculation. For these ten instances the average deviation between the BET and HJ area values is 1.04%. The average deviation for the various gases on the

same solid is 1.42% for the BET and 1.18% for the HJ methods while the average deviation between the means of the BET and HJ areas is 0.85%.

Both isotherm methods described are relative in the sense that they require calibration with respect to a solid of known surface area. With the BET method this calibration consists in the calculation of the average area occupied per molecule in the monolayer. The HJ isotherm method must also be calibrated on a solid of known area and involves further the choice of one of the four constants listed in Table III. In this choice there is no dependence upon any other method provided two or more straight lines are obtained in the HJ plot. If only one straight line is obtained the HJ isotherm method requires further calibration by either an absolute method or the results of a BET calculation.

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Electrical Properties of Solids. XVII. Poly-4-vinylpyridine¹ and Some of its Derivatives^{2,3}

BY WILLIAM N. MACLAY⁴ AND RAYMOND M. FUOSS

The electrical properties of picric acid in poly-4-vinylpyridine have been measured at low frequencies in the range 25–105°. The a.c. loss factor is larger than the sum of dipolar loss factor and the loss computed from the d.c. conductance, by an amount $\Delta\epsilon''$ which varies inversely as the square root of frequency and exponentially as reciprocal absolute temperature. A term $\Delta\epsilon'$, numerically equal to $\Delta\epsilon''$, appears in the dielectric constant as well. The d.c. conductance also increases exponentially with $1/T$. All loss terms increase with increasing plasticizer (dibutyl tartrate) content. Poly-4-vinylpyridine, quaternized with methyl bromide, is a good electrolytic conductor, especially when plasticized.

Introduction

In one⁵ of the preceding papers of this series, solutions of a strong electrolyte (tetrabutylammonium picrate) in a plastic solvent (polyvinyl chloride plasticized with diphenylmethane) were described. The observed loss factors were greater than those computed by adding the losses due to the dipoles of the plastic solvent to the measured d.c. conductance. Simultaneously, an unexpectedly high dielectric constant was found. The excess dielectric constant over that due to the polymer was numerically equal to the excess term in the loss factor, and varied inversely as the square root of frequency. Polyvinylpyridine⁶ resembles other vinyl polymers in its general physical properties, but differs chemically in carrying tertiary nitrogen atoms; these can be converted to positively charged nitrogen atoms by the addition of acid, or of alkyl

halide. We thus have the opportunity of preparing an electrolyte⁷ in which the (multiply charged) cation is simultaneously a polymeric molecule. The purpose of this paper is to present experimental results on "solid" polyvinylpyridinium picrate; qualitatively, the electrical properties closely resemble those of solutions of small electrolytes in plastic solvents. On quaternization with methyl bromide, polyvinylpyridine gives such a highly conducting electrolyte that the a.c. properties cannot be measured in the low frequency range.

Experimental

Materials.—4-Vinylpyridine (ViPy) was freshly distilled (53–54° at 8 mm.) and polymerized in emulsion,⁶ using the recipe: 200 ml. 4-ViPy, 400 ml. water, 0.5 g. Nekal AEMA and 1.0 g. benzoyl peroxide. After four hours at 50°, the emulsion was broken by dilution and the granular precipitate was thoroughly washed with water (16 changes in 3 days). The product was then dried under vacuum at 40°; yield 181 g. Viscosities were measured in alcohol: $C = 0.338$ g./100 ml. solution, $\eta_{sp}/C = z = 5.98; 0.229-5.24; 0.1016 - 4.66$. These data extrapolate linearly to $[\eta] = 4.05$ with $k' = 0.34$.

Poly-4-vinyl-N-methylpyridinium bromide ("polybromide") was prepared by adding 10 ml. of methyl bromide to 10 g. of PViPy in 300 ml. of dimethylformamide. On standing at room temperature several hours (under a Dry Ice reflux), the mixture gelatinized. Addition of 250 ml. of

(1) Project NR 054-002 of the Office of Naval Research, Paper No. 32.

(2) Abstracted from a thesis presented by William N. Maclay to the Graduate School of Yale University in partial fulfillment of the requirements for the Degree of Doctor of Philosophy, June, 1950.

(3) Presented at the Symposium on Polyelectrolytes at the New York Meeting of the American Chemical Society, September 10, 1951.

(4) Davis and Elkins College, Elkins, W. Va.

(5) D. J. Mead and R. M. Fuoss, *THIS JOURNAL*, **67**, 1566 (1945).

(6) E. B. Fitzgerald and R. M. Fuoss, *Ind. Eng. Chem.*, **42**, 1603 (1950).

(7) R. M. Fuoss, *Science*, **108**, 545 (1948).

methanol liquefied the gel; the solution was poured into 2 l. of rapidly stirred anhydrous dioxane. A high speed counter-rotating stirrer (Brookfield Engineering Laboratories, Stoughton, Mass.) was used; it completely prevented the exasperating gum formation which so frequently plagues this operation. The white precipitate was washed with dioxane and dried under vacuum at 40°. The salt was titrated potentiometrically in methanol solution against 0.0616 *N* silver nitrate in methanol, using a silver wire and a glass electrode. Found: Br, 35.15, 35.18; calcd., Br, 39.96; 88% quaternization. Methanol was used because silver bromide does not precipitate from dilute aqueous solutions of the polybromide on addition of silver nitrate solution; apparently the polysalt (polybromide, polynitrate or a mixture) peptizes silver bromide. Acidification with nitric acid causes turbidity to appear gradually. Incidentally, one batch of salt prepared as above was allowed to stand under dioxane for several days: it became yellow, turned light green on drying and gave a dark green solution (22 g. of salt in 300 ml.) in methanol. On a second precipitation into 2 l. of fresh dioxane, a colorless precipitate was obtained (which also analyzed to 35.17% Br) and the supernatant liquid was colorless.

Another sample of polyvinylpyridine was partially quaternized with methyl bromide; the product is effectively a copolymer of vinylpyridine and vinyl-*N*-methylpyridinium bromide, and will be designated as the "copolymer salt." To 10 g. of PViPy in 300 ml. of dimethylformamide was added 1.8 ml. of methyl bromide. After one hour at room temperature, the mixture tested positive for bromide by potentiometric methods (negative with silver nitrate; *i.e.*, the polymer prevented precipitation of silver bromide) and was poured into one liter of dioxane with rapid stirring. The white precipitate was washed and dried under vacuum at 40°. Potentiometric titration gave 13.59% bromide, corresponding to 34.0% quaternization. The copolymer salt thus has on an average one cationic charge for each six chain carbons.

Plasticizers for PViPy were tested as follows: 0.25 g. of material to be tested were dissolved in 5 ml. of (low boiling) petroleum ether or diethyl ether, and added to 1.0 g. of powdered polymer. The mixture was stirred until the solvent had evaporated, leaving the test material uniformly distributed over the polymer. The mixture was then heated in a small test-tube and examined after heating for 1 hr. at 100°. Rubbery powders were obtained for good plasticizers. Diphenylmethane, diphenyl ether, dimethyl phthalate, dibutyl phthalate, dioctyl phthalate, tricresyl phosphate, methyl isobutyl ketone, heptadecanol, *p,p'*-dioctyl-diphenylamine and tributyl citrate failed to plasticize; carbonyl acetate and methyl *n*-amyl ketone showed a slight plasticizing action; methyl and butyl cellosolve, glycerol monohydroxyacetate, butyl lactate and dibutyl tartrate were good plasticizers.

Preparation of Discs.—Electrical measurements were made on discs 5 cm. in diameter and 3.2 mm. thick. The discs were pressed in a closed type mold, usually, for 6 min. at 165°. The mold had a side tube which was sealed by the top plunger when the mold was completely closed; vacuum applied here during the closing of the mold onto the press powder removed air which otherwise might have been entrapped in the disc. The mold was brought to temperature in a hydraulic press with electrically heated platens and opened; the press powder was quickly added. Vacuum was applied to the side tube at the same time as hydraulic pressure was applied to the mold. The mold was closed slowly (20–30 sec. for 1" stroke); after 6 min., cold water was run through the outer jacket of the mold. It cooled in a few minutes; the disc was then removed. We found that a very thin film of Dow-Corning silicone stopcock grease on the plungers of the mold acted as a very efficient mold release.

In order to test the sensitivity of the electrical properties of PViPy to the heating cycle in the press, a disc for which $\epsilon' = 3.100$, $\tan \delta = 0.0015$ at 25° and 60 cycles was broken up, and the fragments remolded at 165°, 6 min. pressing. The constants were found to be 3.117 and 0.0016; on breaking up and remolding again, we found 3.118 and 0.0016. The original disc was a transparent light yellow; after the third pressing, the material had not darkened noticeably.

Weight, thickness and diameter of the discs were determined, and then tin foil electrodes (0.5 mil) were rubbed on, using a thin film of vaseline as adhesive. Aquadag may not be used; water crazes polyvinylpyridine plastics badly.

The discs were kept in a desiccator to avoid attack by atmospheric moisture.

Picric acid was added to some samples (Table I) by dissolving it in ether, mixing the solution with the powdered polymer and then stirring until the ether had evaporated. Dibutyl tartrate was also added in ether solution in a similar way; after the ether evaporated, the molding powder was placed in an oven at 100° for 15 min. to permit the plasticizer to strike in. If this precaution is not taken, plasticizer will be extruded in the press. We are grateful to the Kessler Chemical Company (State Road and Cottman Ave., Philadelphia 35) for a sample of dibutyl tartrate.

TABLE I
COMPOSITION OF DISCS MEASURED

No.	Polymer	P.A.	DBT	ρ
5	PViPy	0.0	0.0	1.122
6	PViPy	2.0	.0	1.151
7	PViPy	4.2	.0	1.158
8	Polybromide	0.0	.0	1.314
9	PViPy	7.9	.0	1.180
10	PViPy	4.1	7.4	1.142
11	Copolymer	0.0	0.0	1.238
12	PViPy	4.1	25.3	1.175
13	Polybromide	0.0	21.2	1.325

The composition and density of the samples are given in Table I; weight percentages of picric acid and dibutyl tartrate (columns 3 and 4) are reckoned on the weight of polymer. For orientation, 4.05 weight per cent. picric acid on the weight of polyvinylpyridine is 1.86 mole per cent. reckoned on the pyridine nitrogen of the polymer; *i.e.*, about one pyridine in fifty is converted to the pyridinium picrate.

Electrical measurements were made in a guarded copper cell⁸ whose electrodes were faced with platinum. The cell (plus sample) was immersed in an oil-bath, thermostated to $\pm 0.05^\circ$. Capacity and a.c. resistance or loss tangent were measured on a Schering-Wheatstone bridge⁹ and d.c. resistance on a guarded Wheatstone bridge.^{10,5} When the tangent of the loss angle of the sample approached unity as temperature was raised, the cell was shunted by a guarded mica capacitor ($C = 304.6 \mu\mu\text{f}$, $\tan \delta = 0.00025$ at 60 cycles) in order to obtain a satisfactory balance on the Schering bridge, and the characteristics of the sample were computed from the data on the parallel combination and the known constants of the shunt. Then, as temperature was

TABLE II
ELECTRICAL PROPERTIES AT 60 CYCLES OF POLYVINYL-PYRIDINE SAMPLES

	ϵ'		ϵ''		ϵ'		ϵ''	
	No. 5	No. 6	No. 5	No. 6	No. 7	No. 7	No. 9	No. 12
25	3.100	0.0055	3.090	0.0133	3.259	0.0198		
35	3.095	.0062	3.096	.0146	3.269	.0222		
45	3.097	.0088	3.105	.0167	3.278	.0256		
55	3.089	.0080	3.108	.0191	3.295	.0315		
65	3.089	.0096	3.119	.0233	3.311	.0406		
75	3.091	.0117	3.125	.0288	3.324	.0518		
85	3.096	.0146	3.134	.0342	3.362	.0794		
95	3.150	.0463	3.421	.1339		
105	3.183	.0738	3.521	.242		
	No. 9		No. 10		No. 12			
25	4.33	0.105	4.09	0.0727	4.98	0.582		
35	4.42	.152	4.16	.0966	6.28	1.356		
45	4.73	.267	4.26	.1519	8.48	2.90		
55377	4.39	.256	12.33	8.03		
65	5.00	.721	4.66	.540	17.85	27.5		
75	5.54	1.411	5.36	1.391	26.13	105.9		
85	6.42	2.94	7.32	4.50	46.4	266		
95	12.31	18.65	80.6	757		
105	14.22	67.6	18.22	90.3	148.4	2030		

(8) R. M. Fuoss, *Trans. Electrochem. Soc.*, **74**, 91 (1938); R. M. Fuoss, *This Journal*, **63**, 371 (1941).

(9) D. Edelson, W. N. Maclay and R. M. Fuoss, *J. Chem. Educ.*, **27**, 644 (1950).

(10) R. M. Fuoss, *This Journal*, **60**, 451 (1938).

further increased, and the tangent of the combination approached unity, the mica condenser was disconnected, and the bridge shifted to the Wheatstone circuit. Usually, measurements were made at 60, 120, 240 and 480 cycles; for low loss materials, measurements were made at 500 volts. For higher losses, bridge voltage was reduced to prevent heating of the sample by the measuring current.

Results

In order to show the behavior of typical systems, an abstract of the data is presented in Table II. The wide range of the variables makes it impractical to present the results graphically, except on a logarithmic scale. Space limitations prevent inclusion here of the data at all frequencies and temperatures for the systems investigated; the numerical results are available as American Documentation Institute Document No. 3137.¹¹

Discussion

Polyvinylpyridine has about the electrical properties one would expect: a low dielectric constant and loss factor, both relatively insensitive to frequency and temperature. For example, at 25° and 60 cycles, $\epsilon' = 3.100$ and $\epsilon'' = 0.0055$ while at 85° and 60 cycles, $\epsilon' = 3.096$ and $\epsilon'' = 0.0146$. The corresponding figures for 480 cycles are, respectively, 3.087 - 0.0039 and 3.080 - 0.0098. The small loss is probably due to some motion of the polar pyridine groups, but the high viscosity of the plastic prevents much orientation.

When picric acid is added, however, both dielectric constant and loss factor increase at a given frequency and temperature, and more rapidly than proportional to picric acid concentration. At least seven mechanisms are responsible for the in-phase component of current: ionic conductance due to hydrogen ions, picrate ions and polypyridinium ions, and dipole losses due to free picric acid, associated pyridinium picrate and pyridine groups. To this must be added an unknown source⁵ of loss which seems to appear when electrolyte is present in a medium of high viscosity. The dielectric constant is made up of contributions from electronic polarization, picric acid dipoles, associated ion pairs on the polymer chain and pyridine dipoles on the chain; here also an additional unexplained term appears which runs parallel to the anomalous term in the loss factor. When plasticizer is added, the loss factor increases still further, due to the decrease of internal hydrodynamic resistance; the main contributions here are the increased ionic terms. These results are summarized in Fig. 1, where logarithm of 60 cycle loss factor is plotted against temperature; it will be noted that the data cover a range of about five decades in dissipation.

If electrolytic conductance is present, the measured d.c. conductance κ_0 is equivalent to an ionic loss factor

$$\epsilon''_i = 9\kappa_0 \times 10^{12}/5f = a\kappa_0/f \quad (1)$$

We might expect therefore that the total a.c. loss factor ϵ'' of a polar material containing electrolyte would be the sum of ϵ''_i and ϵ''_p where ϵ''_p is the

(11) For detailed tables of data, order Document 3137 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting \$1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or \$1.00 for photocopies (6 × 8 inches) readable without optical aid.

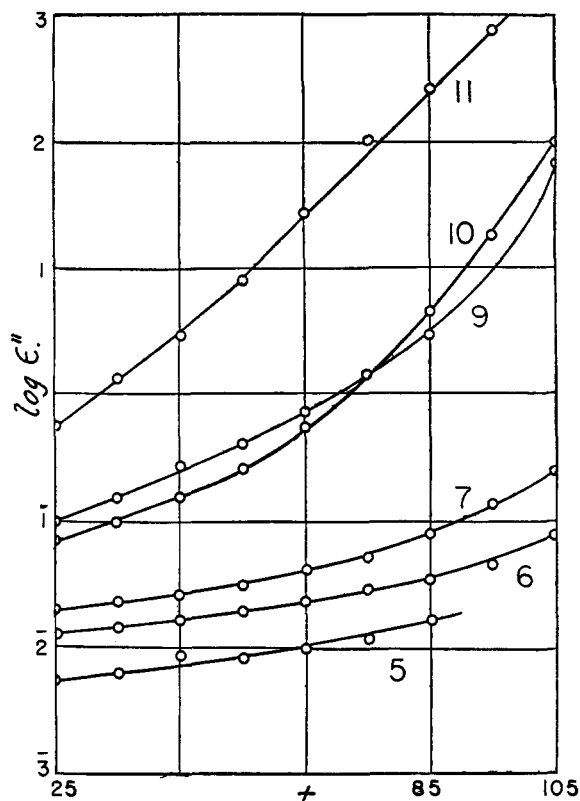


Fig. 1.—Loss factors (at 60 cycles) as functions of temperature.

familiar dipole loss factor arising from relaxation effects. Actually, we find for the systems of Table II

$$\epsilon'' = \epsilon''_i + \epsilon''_p + \Delta\epsilon'' \quad (2)$$

where $\Delta\epsilon''$ is the "extra" term mentioned above. Empirically, it was found⁵ for solutions of tetrabutylammonium picrate in polyvinyl chloride-diphenylmethane that

$$\Delta\epsilon'' = k/\sqrt{f} \quad (3)$$

Furthermore, the increment $\Delta\epsilon''$ in dielectric constant over that of the plastic base was found to be equal to $\Delta\epsilon''$. For the polyvinylpyridinium picrates described here, we find a similar behavior: both ϵ' and ϵ'' are linear in reciprocal root frequency at the higher temperatures as shown in Fig. 2. The slope k of the $\epsilon'f^{-1/2}$ and the $\epsilon''f^{-1/2}$ plots increases rapidly with temperature as shown in the $\log k-1/T$ plot of Fig. 3. The d.c. conductances also increase exponentially with $1/T$; a plot of $\log k$ against $\log \kappa_0$ for No. 12 is linear and from its slope, we find that k varies approximately as the square root of the d.c. conductance. A similar result was found¹² previously for plasticized polyvinyl chloride containing hydrogen chloride.

The d.c. conductance was found to depend on time and on voltage; the polarization effects were in general similar to those observed in the PViCl-Ph₂CH₂ systems. In order to obtain d.c. conductances corresponding to no polarization, the a.c. data were extrapolated to zero frequency by the following procedure. First, ϵ' was plotted against $f^{-1/2}$ to determine k , and $\Delta\epsilon''$ was calculated

(12) R. M. Fuoss, THIS JOURNAL, 61, 2329 (1939); Figs. 6 and 7.

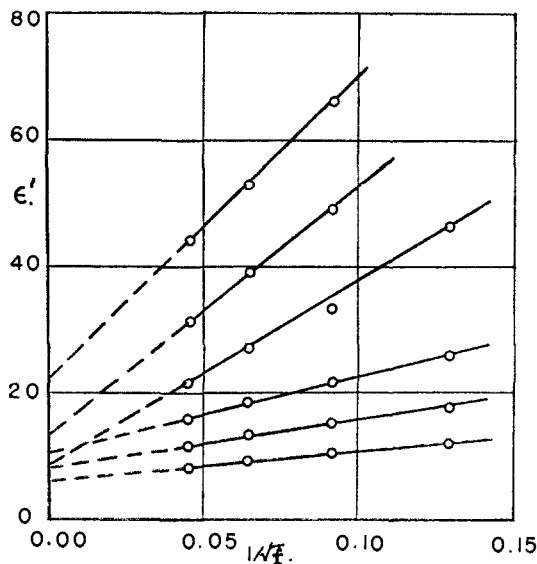


Fig. 2.—Frequency dependence of dielectric constant (No. 12) and determination of k ; top curve, 105° ; bottom curve, 55° .

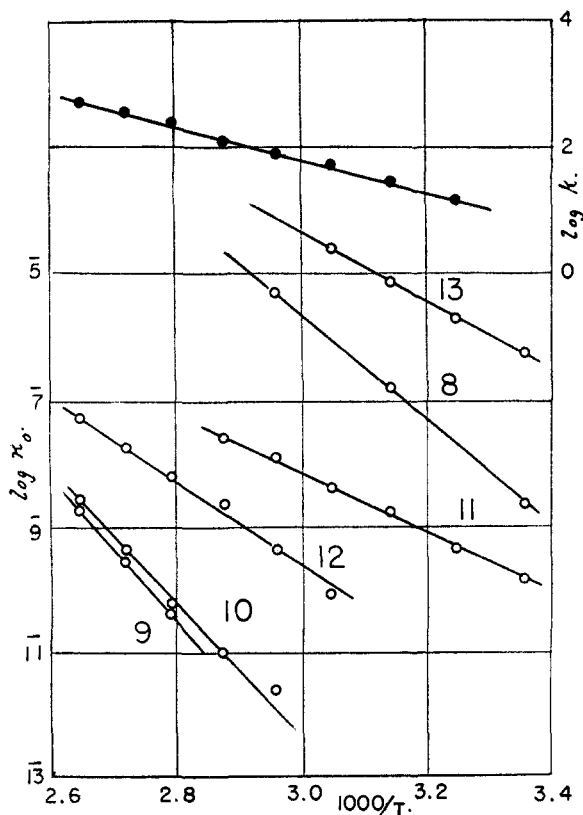


Fig. 3.—Dependence of d.c. conductance on temperature; open circles, ordinates left. Dependence of k (No. 12) on temperature; solid circles, ordinates right.

by Eq. (3). At the higher temperatures, $\epsilon''_p \ll (\epsilon''_i + \Delta\epsilon'')$, so $\Delta\epsilon''$ was then simply subtracted from the total a.c. loss and the difference was computed to κ_0 by Eq. (1). For example, for No. 12, k at 95° was found to be 375 and ϵ'' at 60 cycles was 757. Then $(757 - 375/\sqrt{60}) = 709$, whence κ_0 (calcd.) = 2.36×10^{-8} ; the d.c. conductance

measured at 10 volts was 1.78×10^{-8} after a steady polarization state was reached. At lower temperatures, ϵ''_p can no longer be neglected: in this case, κ_0 calculated by the above method increases with frequency due to the $\epsilon''_p f/a$ term. When ϵ''_p is not changing very rapidly with frequency (as is usually the case for polymeric systems), κ_0 can be determined by plotting κ_0 (calcd.) = $f(\epsilon'' - kf^{-1/2})/a$ against frequency and extrapolating to $f = 0$. Then having determined the d.c. conductance, $a\kappa_0/f$ is subtracted from ϵ'' to obtain the pure a.c. loss ϵ''_p . The two limiting cases where $\epsilon'' \approx \epsilon''_i + \Delta\epsilon''$ and $\epsilon'' \approx \epsilon''_i + \epsilon''_p$ are therefore easy to handle: the first corresponds to higher and the second to lower temperatures. In the intermediate range, it is not always possible to separate the different contributions to the total loss.

The results of these calculations can be summarized as follows. If we consider the system polyvinylpyridine-picric acid-dibutyl tartrate (PVi-Py-PA-DBT), we find that dielectric constant, loss factor and conductance increase with increasing temperature. The curves for ϵ' and ϵ'' are quite complicated, because they are the resultant of so many terms. The dielectric constant shows the characteristic sigmoid increase, on which is superimposed a k/\sqrt{f} term which increases exponentially with $1/T$. The loss factor has a small ϵ''_p term on which are superimposed two exponential terms, arising from κ_0 , and the $\Delta\epsilon''$ term. These two have different exponents, the $\Delta\epsilon''$ term climbing about half as fast (on a logarithmic scale) as the κ_0 term. With increasing plasticizer content, dielectric constant increases because of increased freedom of molecular motion; simultaneously, both κ_0 and $\Delta\epsilon''$ increase very rapidly. If we compare samples 7, 10 and 12 at 105° , for example, we find only a small loss in the unplasticized sample (0.242 at 60 cycles). Addition of 7.4% DBT raises this to 90.3 and at 25.3%, ϵ'' has reached 2030. The latter is mostly ionic; $\Delta\epsilon''$ is 67 and ϵ''_p is probably of order unity. Obviously more data are needed before a detailed analysis of the plasticized systems can be made: the general trends of the electrical properties are, however, at least qualitatively predictable.

In the above materials, the electrolyte was a mixture of polymer picrate and free picric acid; we next investigated some polyelectrolytes in which the pyridine nitrogens attached to the polymer chain were quaternized by the addition of methyl bromide. Because high temperature is required for molding, higher alkyl halides could not be used, due to the ease with which quaternary alkyl salts split out olefin. This gives a system in which the cations are part of the polymer molecule, while the anions are mechanically independent particles. Furthermore, the salt is a strong electrolyte; consequently, we expected to find much higher conductances than in the picrate systems. As a matter of fact, the d.c. conductances of Samples 11, 8 and 13 were so high that a.c. measurements with our present equipment were impossible; it will be necessary to work at considerably higher frequencies. Sample 11 was partially quaternized

(33%) polyvinylpyridine; it was essentially a copolymer of vinylpyridine and N-methyl-4-vinylpyridinium bromide. As seen in Fig. 3, the conductance was much higher even than that of the plasticized picrate. Sample 8 was 88% quaternized; as expected from the higher electrolyte content, the conductance is still higher. Finally, on plasticizing (No. 13), the conductance rose nearly two decades more. These plastic elec-

trolytes have very large positive temperature coefficients of conductance; for No. 13, κ_0 approximately trebles for each 10° rise in temperature. We thus have at our disposal a system of electrolytes whose conductance is of the order of ordinary electrolytic solutions, with the significant difference that they are plastic solids rather than liquids. Further work is in progress.

NEW HAVEN, CONN.

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The Heats of Vaporization and Vapor Heat Capacities of Some Dimethylcyclohexanes¹

By J. P. McCULLOUGH,² W. B. PERSON AND RALPH SPITZER

The vapor heat capacities and heats of vaporization of cyclohexane and four isomeric dimethylcyclohexanes have been measured in a flow calorimeter system. The vapor heat capacity results, in cal. deg.⁻¹ mole⁻¹, may be represented in the range of experimental measurements (approximately 400–500°K.) by the empirical equations

$$\begin{aligned} \text{cis-1,2-Dimethylcyclohexane: } C_p &= -51.34 + 0.34991T - 2.4515 \times 10^{-4} T^2 \\ \text{trans-1,2-Dimethylcyclohexane: } C_p &= -50.96 + 0.35146T - 2.427 \times 10^{-4} T^2 \\ \text{cis-1,3-Dimethylcyclohexane: } C_p &= -57.92 + 0.38060T - 2.764 \times 10^{-4} T^2 \\ \text{trans-1,4-Dimethylcyclohexane: } C_p &= -19.76 + 0.21844T - 1.057 \times 10^{-4} T^2 \end{aligned}$$

A comparison of the experimental heat capacity data with values calculated by the method of methyl increments shows the latter to be significantly high, but the structural concepts involved in the semi-theoretical computation are given further verification by the internally consistent results for the dimethylcyclohexanes.

In view of the continuing need for accurate thermodynamic data a flow calorimeter similar to that used by Waddington, Todd and Huffman³ has been constructed. Their design is well adapted for measuring the vapor heat capacities and heats of vaporization of substances boiling above room temperature.

An important application of thermal data has been in the elucidation of the structures of complex molecules. Beckett, Pitzer and Spitzer⁴ have used the information gained in their study of cyclohexane and methylcyclohexane to compute the heat capacities of the dimethylcyclohexanes. The vapor heat capacities of several dimethylcyclohexanes have been measured in order to determine the reliability of such approximate methods of calculation.

Experimental

Apparatus and Procedure.—Since the flow calorimeter built for this investigation is similar in construction and operation to that described by Waddington, *et al.*,³ only a brief account of the method will be given here.

The vapor heat capacity of a substance is determined by observing its temperature rise when it is passed over an electrical heater at a constant, known rate of flow. The heater and two platinum resistance thermometers are enclosed in a vacuum-jacketed, silvered calorimeter designed to minimize both heat losses and indirect heating effects on the thermometers.³ A thermostated bath surrounds the calorimeter and brings the vapor entering it to a constant temperature. Under these conditions the vapor heat capacity is defined by

$$C_p = W/F\Delta T - h/F\Delta T = C_{p(\text{app.})} - h/F\Delta T$$

where W is the power input of the calorimeter heater, F is

the rate of flow of vapor and h is the heat loss from the calorimeter to its surroundings. Independent values of the temperature rise, ΔT , are obtained from observations with the two thermometers. For a particular mean vapor temperature and a constant ΔT , the heat loss, which is primarily due to radiation, is essentially constant regardless of flow rate. Hence, C_p may be evaluated by measuring $C_{p(\text{app.})}$ ($= W/F\Delta T$) at several rates of flow, plotting $C_{p(\text{app.})}$ vs. $1/F$ and extrapolating the resulting straight line to $1/F = 0$.

The steady flow of vapor required for heat capacity measurements is maintained by boiling the liquid in a vacuum-jacketed, silvered vaporizer located in a second thermostated bath. The vapor is passed through the calorimeter, condensed and returned to the boiler. A relationship between the power input of the electrical boiler heater and the vapor flow rate is determined in separate experiments in which the cycling vapor is diverted to a collection system where it is condensed and trapped in a weighed, detachable receiver. The weight of material produced by a measured quantity of energy during a measured interval of time provides the necessary flow calibration data. By applying suitable corrections to the proportionality thus obtained the heat of vaporization may be computed.³

Waddington and co-workers⁵ have shown that the use of empirical equations of state to calculate $(\partial C_p/\partial P)_T$ is not reliable. They demonstrate that the heat capacity of a hydrocarbon vapor is a linear function of pressure up to one atmosphere and that measurements of C_p at two or more pressures suffice to determine both the heat capacity in the ideal gas state, C_p^0 , and the quantity $(\partial C_p/\partial P)_T$.

Materials.—The dimethylcyclohexanes used in this work were made available by the American Petroleum Institute Research Project 45 at the Ohio State University and the Esso Laboratories of Standard Oil Development Company. The sources and purities of the various samples were

cis-1,2-Dimethylcyclohexane, 99.95 mole % \pm 0.02%	(API RP 45)
trans-1,2-Dimethylcyclohexane, 99.82 mole % \pm 0.08%	(API RP 45)
cis-1,3-Dimethylcyclohexane, 99.85 mole % \pm 0.05%	(API RP 45)
trans-1,4-Dimethylcyclohexane, 99.83 mole %	(Esso Laboratories)

(1) Published with approval of the Monographs Publication Committee, Oregon State College, as Research Paper No. 179, School of Science, Department of Chemistry.

(2) U. S. Bureau of Mines, Petroleum Experiment Station, Bartlesville, Oklahoma. du Pont fellow in chemistry 1947–1948.

(3) G. Waddington, S. S. Todd and H. M. Huffman, *THIS JOURNAL*, **69**, 22 (1947).

(4) C. W. Beckett, K. S. Pitzer and Ralph Spitzer, *ibid.*, **69**, 2488 (1947).

(5) G. Waddington, J. C. Smith, D. W. Scott and H. M. Huffman, *ibid.*, **71**, 3902 (1949). See also earlier references cited there.