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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CHICAGO]

Areas of Carbon Blacks and Other Solids by Gas Absorption[1]

BY M. L. CORRIN

The adsorption isotherms of nitrogen, argon, pentane and pentene-1 have been measured on eight carbon blacks and on rutile and rouge. It is shown that the areas calculated by means of the Brunauer, Emmett and Teller method are self-consistent for the various gases if the area occupied per molecule in the monolayer is determined experimentally on a solid of known area. It is further shown that four condensed films may appear in the isotherm. The use of the HJ isotherm method thus involves a choice of the proper constant. If two or more condensed films are obtained in a single isotherm this choice may be made independently; if only one film is obtained the choice of the proper HJ constant involves a knowledge of the area of the solid as determined by an absolute or the BET method. If the HJ isotherm method is thus modified the results obtained are in excellent agreement with those calculated by the BET method.

In the study of the interaction between carbon blacks and various gases and liquids it is essential that the specific surface areas of the blacks be known, since the several energy quantities which are of interest are expressed significantly in terms of unit surface area. Several methods are available for the estimation of specific surface areas. One of these is the calorimetric or "absolute" method of Harkins and Jura.[2] This method can be employed only with non-porous solids; in its use a correction must be applied for the thickness of the adsorbed film at saturation. This correction requires knowledge of the shape and size distribution of the solid particles and becomes large for solids of high specific area; for solids of low specific area the heat effects are too small for precise measurements. In the calorimetric technique a sensitive calorimeter is required, the liquid is restricted to one exhibiting zero contact angle with the solid and must be thoroughly purified and dried. Few determinations by means of this technique have been reported. Two suitable methods for the determination of specific surface areas are based upon the measurement of the absorption isotherm of a gas on the solid. These are the methods of Brunauer, Emmett and Teller[3] and the isotherm method of Harkins and Jura.[4] Several other methods of calculating the specific area from the adsorption isotherm have been discussed; these will not be considered in this paper.

The adsorption isotherms of nitrogen, argon, pentane and pentene-1 on eight carbon blacks and on rutile and rouge have been determined. From these data the specific surface areas have been calculated by the method of Brunauer, Emmett and Teller (BET) and the isotherm method of Harkins and Jura (HJ). It is shown that if the area occupied per molecule in the monolayer is determined experimentally on a solid of known area the BET method yields results which are consistent for the several gases employed. The HJ method gives consistent areas only if the proper value of the HJ constant is selected; it is shown that more than one HJ constant exists for each solid–gas system. In some instances the selection of the proper constant may be made directly from the HJ plot; in other instances recourse must be had to the results of the BET calculations.

For the purpose of this investigation it is not important if the BET and HJ methods be regarded as resting on a firm theoretical basis or as empirical methods based upon an empirical relation between the specific surface area of the solid and one of the parameters in a two parameter relation describing a portion of the adsorption isotherm.

Experimental

The volumetric method for the determination of adsorption isotherms was employed; the apparatus and manipu-

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[1] (a) This investigation was carried out under the sponsorship of the Reconstruction Finance Corporation, Office of Rubber Reserve, in connection with the Government's synthetic rubber program. (b) For detailed tables of experimental data order Document 3138 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 $1.20 for photocopies (6 × 8 inches) readable without optical aid.

[2] W. D. Harkins and G. Jura, THIS JOURNAL, **66**, 1362 (1944).

[3] S. Brunauer, P. H. Emmett and E. Teller, *ibid.*, **60**, 309 (1938).

[4] W. D. Harkins and G. Jura, THIS JOURNAL, **66**, 1366 (1944).

lations have been described by Emmett,[5] by Harkins and Jura[4] and by Joyner.[6] A constant volume manometer involving an electrical contact, relay and solenoid valve was employed. Pressures were read to 0.05 mm. with a cathetometer.

The purification train for nitrogen consisted of copper screening at 435°, P_2O_5, and a liquid nitrogen trap. The argon supplied by Linde Air Products Company in sealed bulbs was used without further purification. Pentane and pentene-1 were Phillips Research Grade hydrocarbons; they were dried over silica gel, degassed and distilled in high vacuum. All solids were degassed at 400° for 16 hours immediately prior to the adsorption measurements.

The sample of Graphon designated as Graphon (P) was obtained from Professor W. C. Pierce of Pomona College. This material had been treated with hydrogen at 1400°. The rutile was obtained from Dr. R. Dahlstrom of the Titanium Division of the National Lead Company. Rouge was a commercial sample. Spheron 6 and Graphon L2237 were obtained from Godfrey L. Cabot, Inc. The other blacks were supplied by Rubber Reserve.

It was found necessary to store pentene-1 in red glass bulbs and to protect this olefin from mercury vapor with gold foil.

Results and Discussion

The isotherms obtained were with four exceptions normal Type II isotherms; the exceptions were nitrogen and argon on Graphon (P) and Graphon L2237. The isotherms of nitrogen, argon, pentane and pentene-1 on Graphon (P) are shown in Fig. 1. The BET and HJ plots are given in Figs. 2 and 3. The existence of a "hump" in the isotherm of nitrogen on Graphon has been demonstrated previously by Joyner and Emmett.[7]

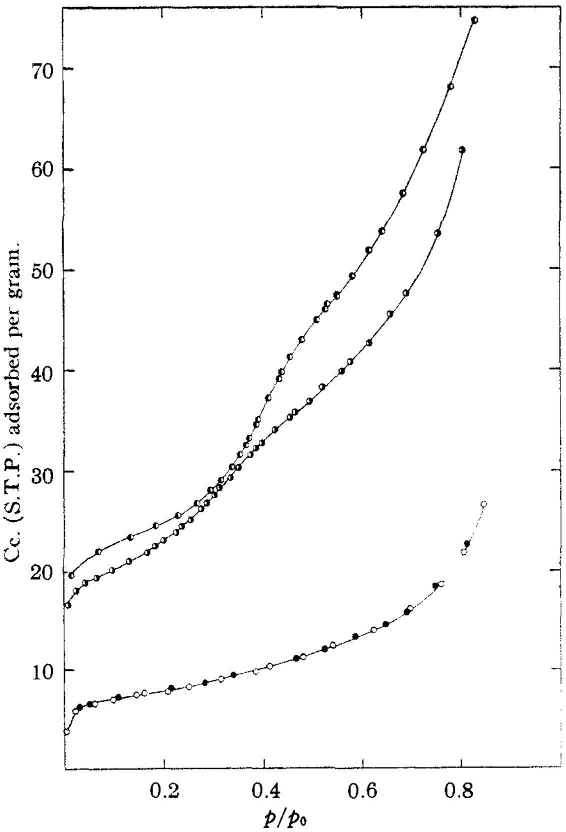

Fig. 1.—Adsorption isotherms on Graphon (P): ◑, nitrogen (−195.8°); ◐, argon (−195.8°); ○, pentane (20°); ●, pentene-1 (20°).

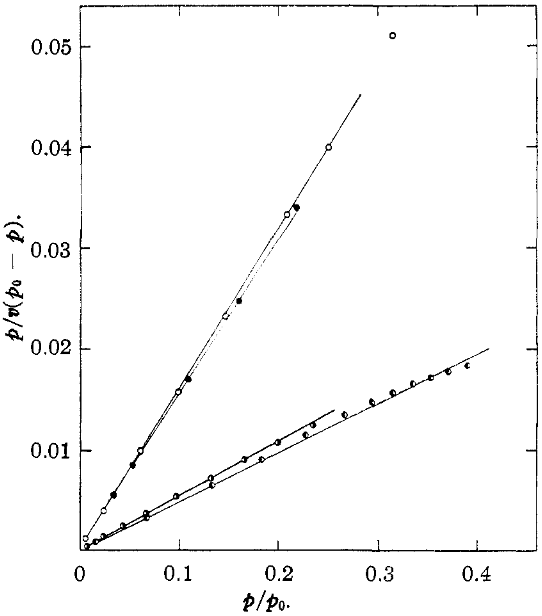

Fig. 2.—BET plots for Graphon (P): ◑, nitrogen (−195.8°); ◐, argon (−195.8°); ○, pentane (20°); ●, pentene-1 (20°).

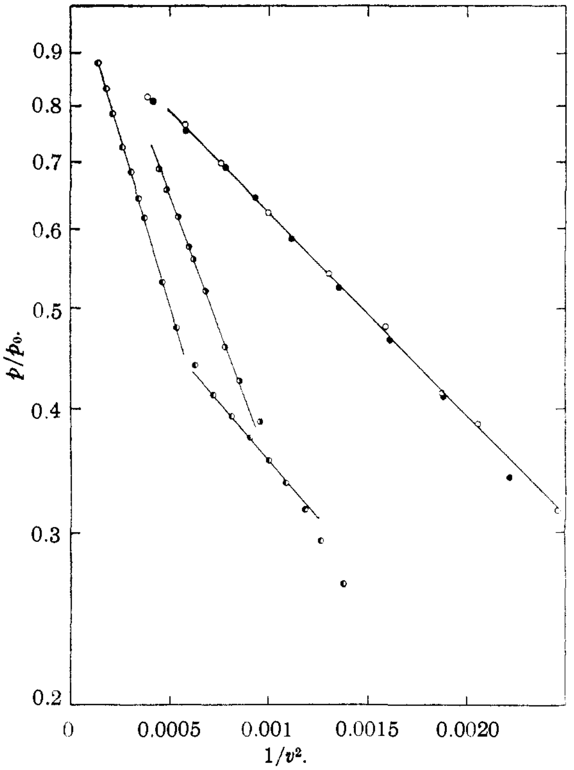

Fig. 3.—HJ plots for Graphon (P): ◑, nitrogen (−195.8°); ◐, argon (−195.8°); ○, pentane (20°), multiply abscissa by ten; ●, pentene-1 (20°), multiply abscissa by ten.

By the BET method one calculates the number of gas molecules required to form a monolayer; from the area occupied per molecule in the mono-

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[5] P. H. Emmett in "Advances in Colloid Science," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1942.

[6] L. C. Joyner in "Scientific Glass Blowing," Instruments Pub. Co., Pittsburgh, 1949.

[7] L. C. Joyner and P. H. Emmett, THIS JOURNAL, **70**, 2353 (1948).

layer the specific surface area of the solid may be calculated. Emmett and Brunauer[8] suggested that the molecular area in the monolayer be computed on the basis of close packing in the liquid or solid; this technique, however, has been shown to lead to inconsistent results for gases other than nitrogen. In this work the area occupied per molecule of adsorbate in the monolayer has been determined experimentally with anatase, the specific surface area of which has been determined by the Harkins and Jura calorimetric method. These areas are listed in Table I and compared to values calculated for close packing in the liquid.

TABLE I

AREAS OCCUPIED IN THE MONOLAYER AS DETERMINED BY ADSORPTION ON ANATASE OF KNOWN AREA AND AS CALCULATED FROM CLOSE PACKING IN THE LIQUID

Gas	σ (exptl.) Å.^{2}	σ (calcd.) Å.^{2}
Nitrogen (−195.8°)	16.2	16.2
Argon (−195.8°)	16.6	14.4
Pentane (20°)	52.3	36.2
Pentene-1 (20°)	49.3	34.9

The quantity of gas required to form a monolayer was calculated by the simple BET equation. The straight line portion of the plot was selected by the following means. The ratios

$$\Delta\left(\frac{p}{v(p_0 - p)}\right)\Big/\Delta(p/p_0)$$

were calculated for adjacent experimental points in the isotherm. The linear region was then taken as that region in which the

$$\Delta\left(\frac{p}{v(p_0 - p)}\right)\Big/\Delta(p/p_0)$$

values scattered at random about some constant value. The best straight line was then calculated by least squares. The areas thus determined are presented in Table II. It will be noted that for a given solid the area as determined by the BET method with the different gases is essentially constant.

Several difficulties present themselves in the application of the HJ method to the determination of specific area. On the purely experimental side the use of $(1/v^2)$, where v is the volume adsorbed, requires considerably more accuracy in the determination of the isotherm to give the same scattering of points about a straight line as obtained in the BET calculation. With the BET method the straight line portion of the plot occurs between relative pressures of 0.05 and 0.2 to 0.3. The straight line portion of the HJ plot is not found in any definite pressure region. In this work the increment ratios of the HJ variables were employed to determine the linear portions of the HJ plot and the best straight lines for these regions calculated by least squares. The square roots of the slopes thus calculated are given in Table II.

TABLE II

BET AND HJ PARAMETERS AND SPECIFIC SURFACE AREAS

	BET method		HJ method				
Adsorbate	Relative pressure range	Σ_{BET}	Σ_{HJ}	Relative pressure range	$A^{1/2}$	k	Film
Rouge							
Nitrogen	0.05–0.25	23.1	24.7	0.25–0.5	5.24	4.72	3
Argon	.04– .27	26.0	24.1	.2 – .8	5.79	4.16	3
Pentane	.08– .26	24.0	23.9	.4 – .6	1.72	13.9	4
Pentene-1	.07– .33	26.1	25.1	.2 – .5	1.72	14.6	3
Rutile							
Nitrogen	0.05–0.25	66.0	64.8	0.15–0.6	15.96	4.06	2
Argon	.02– .25	67.0	68.0	.3 – .5	16.35	4.16	3
			67.3	.5 – .8	17.62	3.82	4
Pentane	.05– .25	67.7	68.1	.1 – .4	5.20	13.1	2
			66.9	.5 – .75	4.81	13.9	4
Pentene-1	.05– .25	66.0	68.7	.15– .4	5.45	12.6	2
			65.9	.4 – .7	4.92	13.4	4
Acetylene black							
Nitrogen	0.05–0.2	65.3	65.0	0.1 –0.2	16.02	4.06	2
			66.4	.2 – .5	14.06	4.72	3
Argon	.05– .25	63.2	62.5	.45– .9	17.56	3.56	2
Pentane	.03– .3	64.7	65.1	.4 – .75	4.68	13.9	4
Pentene-1	.05– .3	64.1	63.9	.3 –. 8	4.77	13.4	4
Philblack O							
Nitrogen	0.05–0.3	81.4	80.2	0.15–0.35	19.76	4.06	2
Argon	.04– .25	80.3	78.1	.04– .2	21.94	3.56	2
			81.2	.25– .5	19.51	4.16	3
			80.0	.5 – .8	20.93	3.82	4
Pentane	0.05–0.3	80.4	80.3	.2 – .8	5.78	13.9	4
Pentene-1	.05– .2	81.9	79.5	.2 – .7	6.31	12.6	2
			81.3	.7 – .9	5.57	14.6	3
Statex K							
Nitrogen	0.05–0.2	79.2	82.0	0.2 –0.5	20.20	4.06	2
Argon	.03– .25	83.0	81.9	.3 – .45	19.69	4.16	3
			80.9	.5 – .85	21.17	3.82	4
Pentane	.03– .25	80.9	83.4	.2 – .7	6.00	13.9	4
Pentene-1	.04– .2	82.3	84.9	.2 – .6	6.74	12.6	2
			82.2	.6 – .9	5.63	14.6	3
Graphon (P)							
Nitrogen	0.01–0.15	85.9	85.6	0.45–0.65	23.58	3.63	1
Argon	.02 –.3	85.3	..	.35– .45	15.51	..	1
	.02– .15		83.1	.5 – .8	26.13	3.18	1
Pentane		84.6	87.3	.4 – .75	6.28	13.9	4
Pentene-1	.05– .15	87.5	84.8	.3 – .8	6.33	13.4	4
Graphon L2237							
Nitrogen	....	..	93.2	0.4 –0.6	22.96	4.06	2
Argon	0.01–0.3	94.3	95.7	.5 – .8	26.88	3.56	2
Pentane	.01– .35	94.9	95.6	.3 – .7	6.88	13.9	4
Pentene-1	.04– .5	96.1	..	....	..	..	..
Kosmobile 77EPC							
Nitrogen	0.03–0.2	111	1110	0.06–0.5	30.34	3.63	1
Argon	.03– .16	112	112	.2 – .65	29.44	3.82	4
Pentane	.03– .25	112	112	.35– .8	7.40	15.1	3
Pentene-1	.03– .2	108	111	.1 – .7	7.60	14.6	3
Spheron 6							
Nitrogen	0.03–0.16	121	122	0.1 –0.35	33.52	3.63	1
			121	.35– .6	29.87	4.06	2
Argon	.02– .2	122	125	.3 – .8	30.02	4.16	3
Pentane	.05– .25	121	121	.2 – .55	7.99	15.1	3
Pentene-1	.05– .2	117	119	.3 – .55	8.90	13.4	4
			..	.55– .8	7.71	..	..
Vulcan 2							
Nitrogen	0.01–0.1	218	..	....	..	..	..
Argon	.01– .2	216	220	0.4 –0.7	61.90	3.56	2
Pentane	.04– .3	210	229	.2 – .4	17.46	13.1	2
			219	.4 – .7	15.76	13.9	4
Pentene-1	.01– .1	218	..	....	..	..	..

The manner in which the linear portions of the BET and HJ plots are selected has a pronounced effect on the area values obtained; this is especially true of the HJ method. The values presented in Table II may thus vary from those obtained by means of the subjective estimation commonly used. In the HJ method the log *p versus* $1/v^2$ relation for films other than condensed may in some regions exhibit only slight curvature and subjectively one can estimate that a straight line exists

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[8] P. H. Emmett and S. Brunauer, THIS JOURNAL, 59, 1553 (1937).

in a region where the increment ratio analysis definitely indicates curvature.

It is apparent that if the square root of the HJ slope, $A^{1/2}$, is simply multiplied by a constant characteristic of each gas to give the specific area, then the areas thus obtained will vary from gas to gas. When more than one linear region exists in the HJ plot one is confronted by the question as to the choice of slopes.

Theoretically the HJ method is based upon a formal analogy between the behavior of monolayers on liquids and of multilayers on solids. In both instances a condensed film is characterized by the relation

$$\pi = -a\sigma + b$$

where π is the film pressure and σ is the total area divided by the number of molecules adsorbed. This may be transformed into an equation between volume adsorbed and pressure by the application of the Gibbs equation to yield

$$\log p = A/v^2 + b$$

It is assumed by Harkins and Jura that A is characteristic only of the gas and the temperature. The experimental fact that in some instances more than one linear region in the log p *vs.* $1/v^2$ plot is obtained suggests that if the HJ treatment is fundamentally valid more than one condensed film must exist and, further, that the constant A must be a function of the nature of the condensed film as well as the nature of the gas and the temperature.

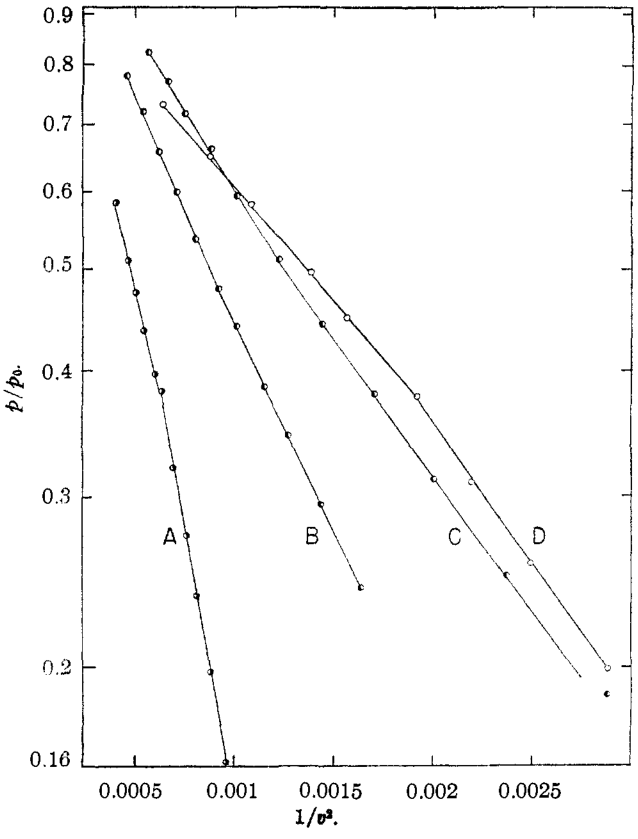

Fig. 4.—HJ plots illustrating some instances in which two straight lines appear: A, nitrogen on Spheron 6; B, argon on Statex K; C, argon on rutile; D, pentane on rutile (multiply abscissa by ten).

In their original paper Harkins and Jura assumed that their method yielded the correct specific areas, and calculated the area occupied per molecule in the monolayer. The distribution with respect to the number of instances observed of areas per molecule thus calculated is not random but shows three peaks. On the basis of the consistent results obtained by the use of the BET method in this investigation it seems more reasonable to ascribe this variation to some systematic deviation in the HJ method. It should be pointed out that the results with nitrogen reported by Harkins and Jura were based upon the use of the linear portion of the HJ plot in the relative pressure region of from 0.2 to 0.4.

Table III

HJ Constants

Adsorbate	Film I	Film II	Film III	Film IV
Nitrogen	3.63	4.06	4.72	4.36
Argon	3.18	3.56	4.16	3.82
Pentane	11.6	13.1	15.1	13.9
Pentene-1	11.2	12.6	14.6	13.4

It had been noted in some unpublished observations by E. Loeser and in this investigation that when two or more straight lines were obtained in the HJ plot the ratios of the square roots of the slopes of these lines fell closely around four values. Three of these values are identical to the ratios that must be assumed for the HJ constants to give the results obtained with nitrogen by Harkins and Jura. It is thus likely that the HJ method is valid in principle but subject to the condition that more than one condensed film may exist for a given solid-gas system. One or more of these condensed films, each described by its characteristic HJ constant, may appear in a given isotherm. In order to apply the HJ method it becomes necessary that the film observed be characterized and the proper HJ constant employed. Some examples of HJ plots in which two straight lines appear are given in Fig. 4.

It is possible on the basis of four condensed films to deal with the data obtained in this investigation. If these films be labeled I–IV in the order in which they appear with increasing relative pressure, the HJ constants may be calculated from the results of the measurements on anatase and the observed ratios of the slopes of the HJ straight lines. These ratios can be determined only in those instances in which more than one straight line is obtained in the HJ plot. In the calculations given here these ratios have been averaged for the various instances observed. The results indicate that on the basis of the information available the ratios of the HJ constants are independent of the nature of the gas. The various HJ constants thus calculated are listed in Table III. That constant characteristic of the film observed on anatase is underlined. The ratios between constants of the various films are K_I/K_{II}, 0.894; K_I/K_{III}, 0.769 and K_I/K_{IV}, 0.833. The area values listed in Table II were calculated with the above constants; the agreement between the BET and the HJ values is considered satisfactory.

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.

Acknowledgments.—The author is indebted to Professor William D. Harkins and to Paul R. Basford for many stimulating discussions.

CHICAGO 37, ILL. RECEIVED DECEMBER 2, 1950

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

Electrical Properties of Solids. XVII. Poly-4-vinylpyridine[1] and Some of its Derivatives[2,3]

BY WILLIAM N. MACLAY[4] 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 one[5] 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. Polyvinylpyridine[6] 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 electrolyte[7] 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

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[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).