The agreement of the data with the Debye–Hückel expression (equation 13) is surprisingly good considering that $\Delta(Z_i^2)$ is extremely large, that the ionic strength range covered is large, that highly charged ions are involved, and only one parameter ($\mathring{a}$) is used. Furthermore, the numerical value of the parameter $\mathring{a} = 6.0$ Å. is quite reasonable if compared with those used to represent activity coefficients of simple electrolytes and if compared with the parameter $\mathring{a} = 7.5$ Å. used to represent $K(\mathrm{IV})_a$ where the average charge of the ions was higher. It thus appears that considerable confidence can be placed in the use of the Debye–Hückel expression (equation 13) for estimation of activity constants for equilibria involving highly charged ions.

OAK RIDGE, TENNESSEE RECEIVED JULY 28, 1950

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[CONTRIBUTION FROM THE RESEARCH LABORATORY, GODFREY L. CABOT, INC.]

# Heats of Adsorption on Carbon Black. III

BY M. H. POLLEY, W. D. SCHAEFFER AND W. R. SMITH

The heats of adsorption of *n*-decane and dihydromyrcene have been measured at 100° on a series of furnace and channel carbon blacks. With one exception, the results obtained are in line with those previously determined with lower molecular weight hydrocarbons at 0°. The adsorption appears to be physical in nature and initial values between 2 and 3 kcal. per $CH_2$ group in the adsorbate were obtained for the heat of adsorption. Dihydromyrcene appears to undergo some degree of reaction with the chemisorbed oxygen complex present on the surface of channel blacks. Since this reaction was not observed when other reinforcing carbon blacks were used as adsorbents, it may be concluded that this is not of primary significance in reinforcement.

The differential heats of adsorption of a number of adsorbates on several carbon blacks have been determined calorimetrically in an attempt to correlate the surface activity of these blacks and their varying efficiency in rubber reinforcement. Previous publications have described the adsorption of elementary gases at $-195°$,[1] and of $C_2$ to $C_5$ paraffinic and olefinic hydrocarbons at 0°.[2,3] In each case the adsorption proved to be van der Waals in nature, and the surface activities revealed by the calorimetric measurements approximated the rubber reinforcing ability of the carbon black adsorbents.

None of the adsorbates studied possessed the two alpha methylene groups characteristic of the unsaturation pattern of natural rubber. These groups have been designated as active in such chemical reactions of rubber as oxidation and vulcanization.[4] Consequently, if chemical bonds between elastomer and carbon black were a factor in reinforcement, such reaction should become apparent when a hydrocarbon possessing these active methylene groups is adsorbed on carbon black at 100°. Dihydromyrcene (2,6-dimethyl-2,6-octadiene) is the simplest hydrocarbon possessing a structure and unsaturation pattern analogous to natural rubber; consequently, it was selected as the adsorbate in the present study. *n*-Decane was used concurrently to provide a reference adsorbate which would isolate the effect of the dihydromyrcene unsaturation.

Preliminary results with a fully reinforcing channel black, Spheron 6, as the adsorbent have been recently reported.[5] In the present paper, measurements have been extended to include additional carbon blacks of varying rubber reinforcing ability.

## Experimental

Research grade *n*-decane was obtained from Eastman Kodak Company and was used without further purification. The dihydromyrcene was prepared by the reduction of geraniol with sodium and ethyl alcohol in liquid ammonia.[6]

The following commercial grades of carbon black were employed as adsorbents: Spheron 6, a medium processing channel black; Vulcan 3, a high abrasion furnace black; and Sterling S, a semi-reinforcing furnace black. In addition three modifications of Spheron 6 were prepared for this work. A Spheron 6 sample was "devolatilized" by heating to 925° in a vacuum for a period of 3.5 hours to free the surface of the chemisorbed oxygen complexes which constitute "volatile" matter.[7] This treatment raised the water sludge *p*H[8] of Spheron 6 from 4.1 to 8.7. The second modification was Graphon, *i.e.*, Spheron 6, which had been partially graphitized at 3200°. The third was a sample of Spheron 6 on which the surface acidic complexes[7] were neutralized by titrating a slurry of Spheron 6 in 1 *N* KCl with 0.1 *N* KOH to a *p*H of 10.0. After titration, the black was washed with boiling distilled water, to reduce the chloride ion contamination, until the *p*H was reduced to 6.0. The titration was then repeated in a water slurry to a *p*H of 8.5 to assure complete neutralization of the surface groups. The black was finally oven dried at 110°. Prior to each adsorption run the carbon black was outgassed in the calorimeter for two hours at room temperature and then for three hours at 250°.

The calorimeters used in this study have been previously described.[2,3] The reference junction was a solid copper cylinder, 7 mm. × 10 mm., to which one junction of the copper–constantan couple was silver soldered. This junction was sealed in a Pyrex bulb connected to the vacuum line and helium supply so that rapid thermal equilibrium with the bath at the beginning of each run could be attained.

The adsorption apparatus was designed for use with hydrocarbon vapors at 100°. The vapor supply bulb, buret, calorimeter, and reference junction were completely immersed in a circulating oil-bath thermostatically controlled to 100 ± 0.015° by a mercury–xylene type thermoregulator in conjunction with a cold-cathode tube relay.[9] All por-

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[1] R. A. Beebe, J. Biscoe, W. R. Smith and C. B. Wendell, Jr., THIS JOURNAL, **69**, 95 (1947).

[2] R. A. Beebe, M. H. Polley, W. R. Smith and C. B. Wendell, Jr., *ibid.*, **69**, 2294 (1947).

[3] R. A. Beebe, G. L. Kington, M. H. Polley and W. R. Smith, *ibid.*, **72**, 40 (1950).

[4] E. H. Farmer, "Advances in Colloid Science," edited by H. Mark and G. Whitby, Vol. II, Interscience Publishers, Inc., New York, N. Y., 1946.

[5] W. D. Schaeffer, M. H. Polley and W. R. Smith, *J. Phys. Colloid Chem.*, **54**, 227 (1950).

[6] E. Chablay, *Ann. Chim.*, **8**, 145 (1917).

[7] W. R. Smith and W. D. Schaffer, "Proceedings of the Second Rubber Technology Conference," edited by T. R. Dawson, W. Heffer & Sons, Ltd., Cambridge, England, 1948, p. 410.

[8] W. B. Wiegand, *Ind. Eng. Chem.*, **29**, 953 (1937).

[9] C. E. Rudy, Jr., and P. Fugassi, *Ind. Eng. Chem., Anal. Ed.*, **12**, 757 (1940).

tions of the adsorption line external to the bath were of 2 mm. capillary and were wrapped with chromel heater ribbon, and insulated with asbestos paper. The temperature of this portion of the line, constituting less than 5% of the total volume, was manually controlled to 120 ± 1° to prevent vapor condensation. The pressure in the buret and calorimeter was read with two similarly heated quartz Bodenstein gages. Pressure readings were reproducible to ±0.15 mm. A cellulose acetate-polyethylene glycol stopcock lubricant, similar to that described by Pearlson,[10] was used on all heated stopcocks in contact with hydrocarbon vapor.[11]

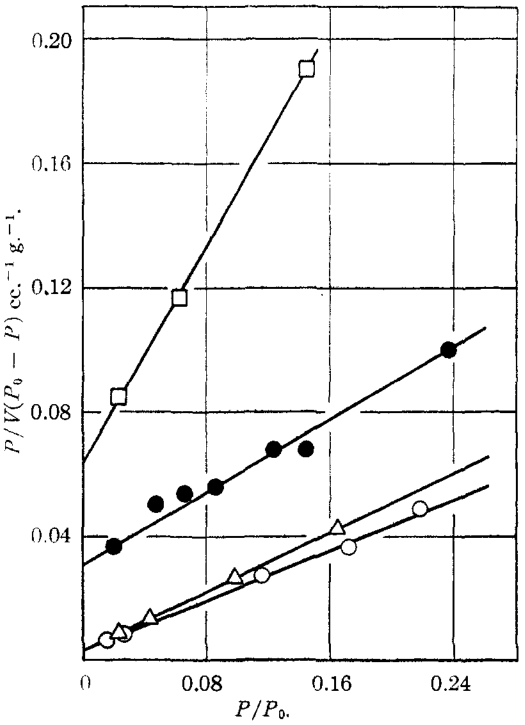

Fig. 1.—B.E.T. plots, *n*-decane at 100°: ○, neutralized Spheron 6; △, Vulcan 3; ●, Graphon; □, Sterling S.

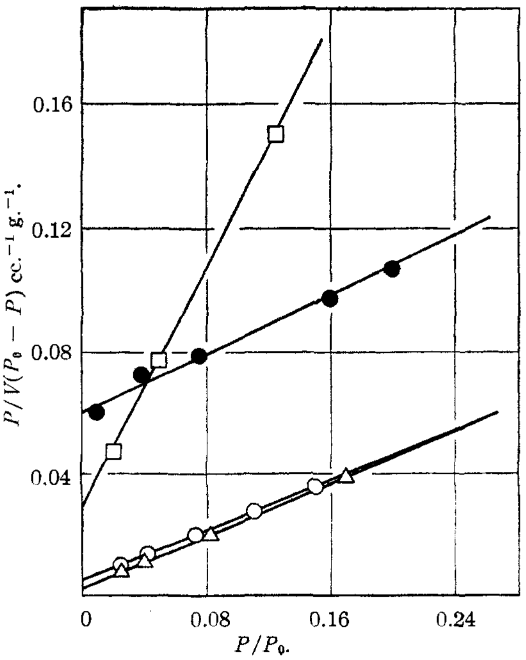

Fig. 2.—B.E.T. plots, dihydromyrcene at 100°: ○, neutralized Spheron 6; △, Vulcan 3; ●, Graphon; □, Sterling S.

## Results and Discussion

The B.E.T. plots for the adsorption of *n*-decane and dihydromyrcene at 100° for the various carbon black adsorbents are presented in Figs. 1 and 2. The cross sectional areas of the *n*-decane and dihydromyrcene molecules on the various carbon black surfaces, as tabulated in column 6 of Table I, have been calculated both from the nitrogen and electron micrograph surface areas. The differences may be ascribed to surface roughness.[12] Since it is unlikely that the same extent of carbon surface is available to these hydrocarbon molecules as to the smaller nitrogen molecule, the proper cross sectional area must lie between these values. An average area of 86 sq. Å. for *n*-decane, and 82 sq. Å. for physically adsorbed dihydromyrcene is proposed. For dihydromyrcene adsorbed on Spheron 6, the value 69 sq. Å. is reasonable, since in this instance limited chemisorption may be involved. The values reported for physically absorbed dihydromyrcene and *n*-decane on Sterling S are not reliable because of experimental uncertainties arising from the low $V_m$ values.

The heat of adsorption, $E_1$, calculated from the simple B.E.T.[13] equation, and the calorimetrically measured values at the completion of the monolayer are in agreement. This has also been noted in all our earlier data both at −195°[1] and at 0°.[2] Brunauer, Emmett and Teller[13] define the heat of adsorption, $E_1$, as obtained from a B.E.T. plot as "the average heat of adsorption for the less active part of the adsorbing surface." From this definition there is no *a priori* reason to identify the B.E.T. value with the calorimetrically determined heat at the completion of the monolayer. Nevertheless, the agreement appears to extend over such a wide range of adsorbents and adsorbates that it is difficult to dismiss it as fortuitous. Agreement has been noted only when the adsorption process is reversible. When something other than physical adsorption is involved the calorimetric heats at the completion of the monolayer are considerably higher than those predicted by the B.E.T. procedure.

The "initial heats" ($V/V_m = 0.05$) for dihydromyrcene on Spheron 6, as shown in Fig. 3, are some 20 kcal. per mole higher than those obtained for *n*-decane on Spheron 6 or for either dihydromyrcene or *n*-decane on "devolatilized" Spheron 6. Subsequent heat of adsorption measurements with dihydromyrcene on the same sample of Spheron 6 made after evacuation for 5.5 hours at 250° and again after 10 hours at 250° markedly decreased the initial heat values, indicating that active sites were either destroyed or were not freed of adsorbate. Electrical calibration and *n*-decane time–temperature curves were characterized by a rapid evolution of heat followed by a slow cooling process. However, when dihydromyrcene was adsorbed on Spheron 6, the rapid initial heat evolu-

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[10] W. H. Pearlson, *Ind. Eng. Chem., Anal. Ed.*, **16**, 415 (1944).

[11] M. H. Polley, *Anal. Chem.*, in press.

[12] R. B. Anderson and P. H. Emmett, *J. Appl. Phys.*, **19**, 367 (1948).

[13] S. Brunauer, P. H. Emmett and E. Teller, This Journal, **60**, 309 (1938).

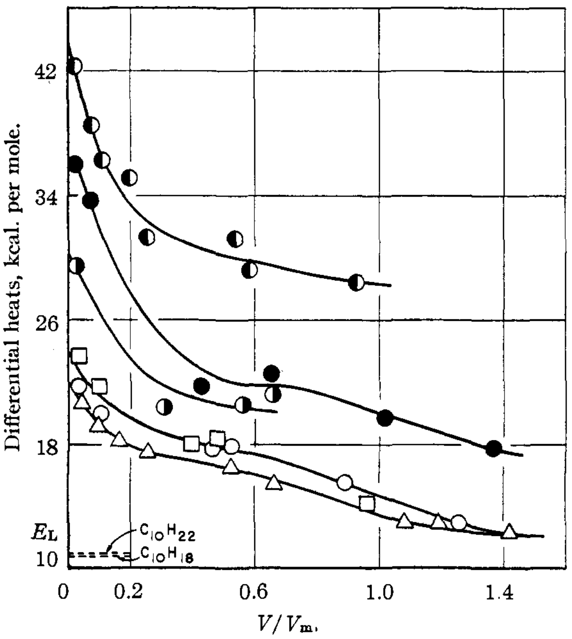

Fig. 3.—Heats of adsorption at 100° (dihydromyrcene on Spheron 6): ◐, Run 79; ●, Run 80; ◑, Run 81; (dihydromyrcene on devolatilized Spheron 6): △, Run 73; (*n*-decane on Spheron 6): ○, Run 77; (*n*-decane on devolatilized Spheron 6): □, Run 71.

tion was followed by a steady slow evolution over a period of some 15 minutes. This cannot be due to diffusion or other experimental features, since, if this were the case it also should have been noted in the *n*-decane runs. It appears that in the adsorption of dihydromyrcene on standard Spheron 6 a rate process is involved. The difference in magnitude of the initial heats of adsorption of the *n*-paraffins and dihydromyrcene may be seen in Fig. 4 where the heat of adsorption at 0.05 $V/V_m$ has been plotted as a function of the number of carbon atoms in the hydrocarbon chain. The $C_3$ to $C_5$ data were obtained at 0°[2,3] and the $C_{10}$ data at 100°. The initial heats are roughly twice the heat of vaporization, a ratio normally obtained for van der Waals adsorption; whereas, the value for dihydromyrcene is almost four times as large.

For clarity, only one run has been plotted for each system in Figs. 5 and 6. Additional runs on the same sample of carbon black produced duplicate results within a precision of 5%, indicating the reversibility of the adsorption. The heats of adsorption of both adsorbates on the "neutralized" Spheron 6 correspond to those on devolatilized Spheron 6. Thus the high heats of adsorption of dihydromyrcene on standard Spheron 6 may be attributed to acidic surface complexes. Unfortunately, chemical and physical definition of the adsorption product has not been achieved. If dihydromyrcene had cyclized when adsorbed on the acidic surface, as it is reported to do in the presence of weak organic acids,[4] the cyclized product should desorb as easily as the original dihydromyrcene since their boiling points differ by only two degrees.[14] The partial irreversibility of the adsorption process then suggests that either an intermolecular structure is formed between the dihydromyrcene and the carboxyl surface oxides[7] or a limited polymerization and cyclization is instigated by these groups on the surface of the black. Since similar surface oxides are present on the furnace blacks, Vulcan 3 and Sterling S, although in much smaller quantities than on Spheron 6, the van der Waals adsorption of dihydromyrcene on these furnace blacks suggests that a critical concentration of surface carboxyl groups exists below which the "chemisorption" of dihydromyrcene either does not occur or does so in amounts too small to be detected.

The differential heat curves of *n*-decane and dihydromyrcene adsorbed on Graphon follow the previously established pattern[1,2] of low initial activity and relatively high heat values at 0.6 to 1.0 $V/V_m$. Comparison of the crystallite dimensions of Graphon and Spheron 6[15] suggests that the large number of low energy sites on the Graphon surface corresponds to the increased proportion of graphite basal plane area. This increased homogeneity permits coöperative condensation even at fairly low pressures,[16] accounting for the high heat values observed near the monolayer coverage. This interaction factor, neglected in the B.E.T. derivation, may be responsible for the deviation observed in the case of Graphon (Table I), when correlation of the B.E.T. and calorimetric heat at the monolayer coverage is attempted.

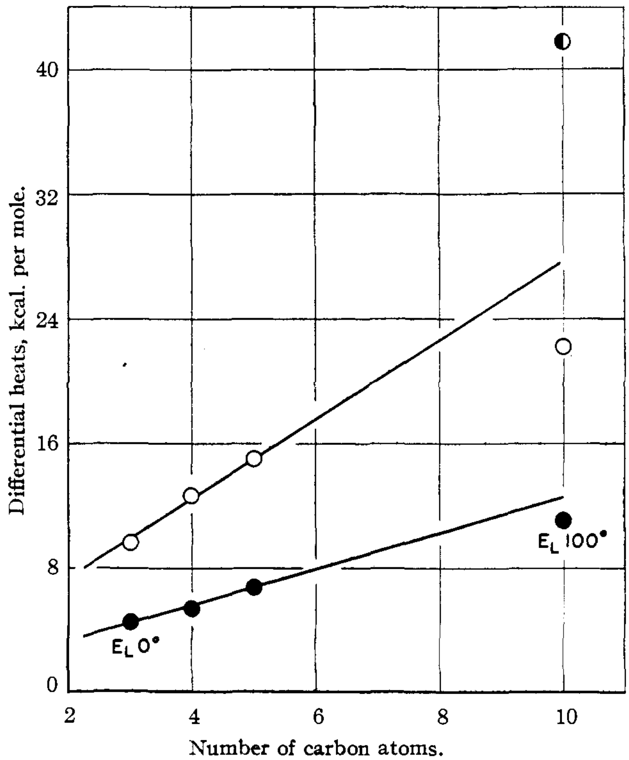

Fig. 4.—Initial heats of adsorption as a function of chain length, normal paraffins and dihydromyrcene on Spheron 6: ◐, dihydromyrcene; ○, paraffins; ●, heats of liquefaction.

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[14] J. L. Simonsen, "The Terpenes," Vol. I, Cambridge University Press, Cambridge, England, 1947, pp. 10, 111.

[15] J. Biscoe and B. E. Warren, *J. Appl. Phys.*, **13**, 367 (1942).

[16] G. D. Halsey, Jr., *J. Chem. Phys.*, **16**, 985 (1948).

TABLE I

| Adsorbent | $N_2$ surface area M.²/g. | E. M. surface area M.²/g. | Adsorbate | $V_m$ cc./g. | σ sq. Å. $N_2$ | σ sq. Å. E. M. | B.E.T., $E_1$ kcal./mole | Calorimetric $E_1$ at $V_m$ kcal./mole |
|---|---|---|---|---|---|---|---|---|
| Spheron 6 | 121 | 106 | *n*-Decane | 4.7 | 95 | 84 | 14.0 | 14.6 |
| Spheron 6 | | | Dihydromyrcene | 5.7 | 79 | 69 | 13.0 | 28.0 |
| Spheron 6 | 112 | 106 | *n*-Decane | 4.9 | 86 | 80 | 13.9 | 14.6 |
| "devolatilized" | | | Dihydromyrcene | 5.0 | 84 | 79 | 13.8 | 13.6 |
| Spheron 6 | 109 | 106 | *n*-Decane | 4.7 | 86 | 84 | 14.2 | 14.3 |
| "neutralized" | | | Dihydromyrcene | 5.0 | 82 | 79 | 13.4 | 14.3 |
| Vulcan 3 | 96 | 90 | *n*-Decane | 4.1 | 87 | 82 | 14.3 | 14.8 |
| Vulcan 3 | | | Dihydromyrcene | 4.5 | 79 | 75 | 14.2 | 14.3 |
| Graphon | 75 | ... | *n*-Decane | 3.1 | 90 | .. | 12.8 | 17.1 |
| Graphon | | | Dihydromyrcene | 3.3 | 85 | .. | 12.0 | 13.6 |
| Sterling S | 21 | 26 | *n*-Decane | 1.0 | 78 | 97 | 13.2 | 13.0 |
| Sterling S | | | Dihydromyrcene | 1.0 | 79 | 97 | 13.4 | 12.9 |

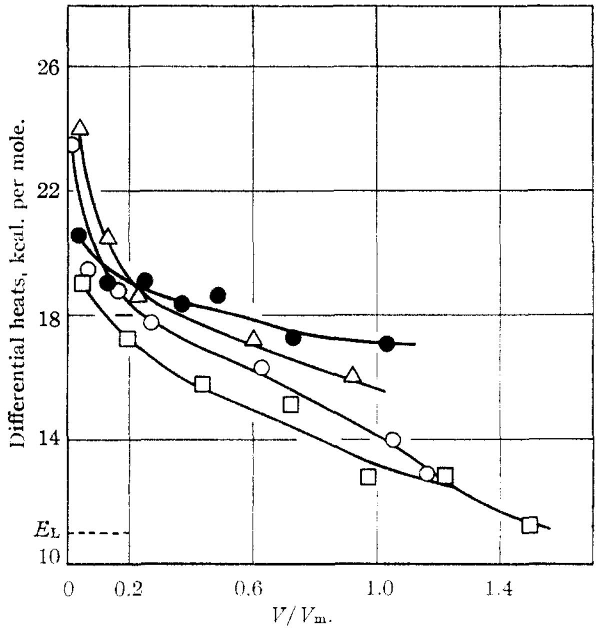

Fig. 5.—Heats of adsorption, *n*-decane at 100°: ○, neutralized Spheron 6; △, Vulcan 3; ●, Graphon; □, Sterling S.

**Conclusion.**—As far as our measurements reveal, the association between hydrocarbons and carbon black is physical in nature, with the single exception that has been noted. While these data have extended only to the $C_{10}$ hydrocarbons, there is no reason to expect that a carbon black surface can distinguish or will respond differently toward a methylene group or a pair of double bonds whether they exist in a 10 or 10,000 carbon atom chain. Accordingly, we suggest that in reinforcement, the association between carbon black and rubber is physical in nature and does not involve highly localized covalent cross linking. It is doubtless essential that a reinforcing pigment offer some degree of restriction to the rubber network and from the present data it appears that van der Waals forces of the order of some 2 to 3 kcal. per $CH_2$ are adequate to provide such restriction.

It should be emphasized that the evidence of chemisorption noted in the adsorption of dihydromyrcene on Spheron 6 cannot be interpreted as a factor in reinforcement, since it was not observed when oxygen complexes were removed from the black nor was it observed when the high abrasion furnace black, Vulcan 3, was used as an adsorbent. While these blacks are very low in volatile content they are still fully reinforcing. The interaction of dihydromyrcene with the surface complexes, *i.e.*, volatile matter, may be associated with the marked retarding effects which channel blacks display in the vulcanization of fully compounded rubber stocks.

If the association between filler particle and rubber is physical in nature, differences between reinforcing and non-reinforcing pigments must be differences in degree rather than kind. To correlate these differences with reinforcement one must consider the magnitude of the heats of physical adsorption at low surface coverage. We have shown in previous publications,[1,2] as well as in Fig. 5 of the present paper, that fully reinforcing channel blacks (Spheron 6) and furnace blacks (Vulcan 3) display higher initial heats of adsorption than semi-reinforcing blacks (Sterling S) and graphitized carbon blacks (Graphon). On the other hand, other pigments usually identified as non-reinforcing, titanium dioxide for example,

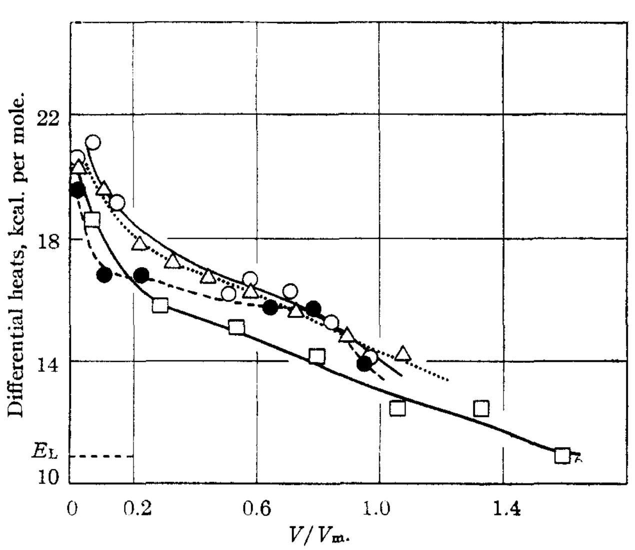

Fig. 6.—Heats of adsorption, dihydromyrcene at 100°: ○, neutralized Spheron 6; △, Vulcan 3; ●, Graphon; □, Sterling S.

display an initial heat of adsorption toward nitrogen[17] comparable to that of the reinforcing channel blacks. Such materials, however, usually do not approach the large extent of surface displayed by carbon black. On the basis of these data one must conclude that high surface activity involving van der Waals forces, together with a high degree of sub-division, are the most significant factors in the reinforcement of rubber by pigments.

**Acknowledgment.**—We are greatly indebted to Dr. Ralph A. Beebe of Amherst College for helpful discussions of this work, and to Dr. Leslie Joyner of Mellon Institute for suggesting the use of ion exchanged or neutralized Spheron 6.

BOSTON 11, MASS. RECEIVED AUGUST 2, 1950

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[17] G. L. Kington, R. A. Beebe, M. H. Polley and W. R. Smith, THIS JOURNAL, **72**, 1775 (1950).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF HARVARD UNIVERSITY AND THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

# Polarographic Characteristics of +2 and +3 Vanadium. II. Polarography in Complexing Solutions[1]

BY JAMES J. LINGANE AND LOUIS MEITES

Data are presented on the half-wave potentials and diffusion current constants of the waves of +2 and +3 vanadium in benzoate, carbonate, citrate, cyanide, fluoride, phosphate, phthalate, pyridine, pyrophosphate, salicylate, tartrate, tetraborate, thiocyanate and thiosulfate solutions.

## Introduction

This paper is an extension of previous work[2-4] on the polarography of +2 and +3 vanadium. The first paper in the present series discussed the polarographic characteristics of vanadous and vanadic ions in dilute solutions of acids and alkalies, acetate buffers and the halides: this paper discusses the ionic states and polarographic behaviors of the complexes formed by these ions in a wide variety of media.

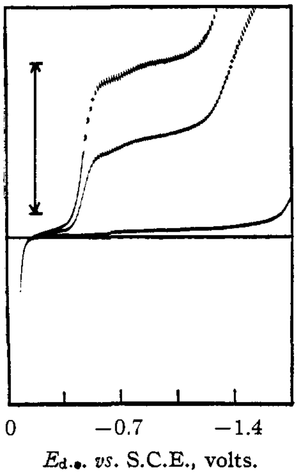

Fig. 1.—Polarograms of (a) 0, (b) 1.83 and (c) 3.44 m$M$ +3 vanadium in 1 $F$ ammonium thiocyanate. The height of the arrow corresponds to ten microamperes.

## Data and Discussion

Of the fourteen complexing agents used in this study, only three were found to give vanadium(II–III) couples which approach thermodynamic reversibility at the dropping electrode. These three systems will be discussed in some detail, together with a few others with unusual polarographic characteristics. Data on the others are summarized in Table I.

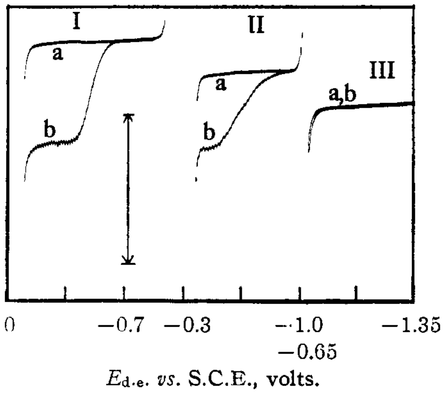

Fig. 2.—(I) Polarograms of (a) 0 and (b) 2.05 m$M$ +2 vanadium in 1 $F$ ammonium thiocyanate. (II) Polarograms of (a) 0 and (b) 1.85 m$M$ +2 vanadium in 1 $F$ sodium thiosulfate. (III) Polarograms of (a) 0 and (b) 1.40 m$M$ +2 vanadium in 1 $F$ potassium cyanide. The height of the arrow corresponds to six microamperes.

Figure 1 and curves I of Fig. 2 are polarograms of +3 and +2 vanadium in 1 $F$ ammonium thiocyanate. The solutions of +3 vanadium are initially very deep green, but change to yellow-green suspensions within a few minutes, while an initially intense lavender vanadium(II) solution soon develops a turbidity and becomes decolorized. In this medium +3 vanadium gives a single cathodic wave (Fig. 1), for which $E_{1/2} = -0.461$ v. (all potentials are referred to the saturated calomel electrode unless otherwise indicated), $I = 1.78 \pm 0.01$, and $\Delta(-E_{d.e.})/\Delta \log [i/(i_d - i] = 65$ mv., in good agreement with the value expected for a reversible one-electron reduction.[5] The corresponding data for the vanadium(II) complex are −0.465 v., −2.04 ± 0.02, and −69 mv. The two half-wave potentials are so close together that the irreversibility of the $V^{+2}$–$V^{+3}$ couple must be very small, and their mean, −0.217 v. *vs.* the normal hydrogen electrode, must be within a few millivolts of the true standard potential. From this value we calculate the figure 2.4 for the ratio of the dissociation constants of the complexes $K_{V(SCN)_m^{3-m}}/K_{V(SCN)_n^{2-n}}$. As neither of the half-wave potentials is altered by changing the thio-

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[1] This paper is based in part on a thesis submitted by Louis Meites to the Graduate Faculty of Harvard University in partial fulfillment of the requirements for the degree of Doctor of Philosophy in February, 1947.

[2] J. J. Lingane, THIS JOURNAL, **67**, 182 (1945).

[3] J. J. Lingane and L. Meites, *ibid.*, **69**, 1021 (1947).

[4] J. J. Lingane and L. Meites, *ibid.*, **70**, 2525 (1948).

[5] I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941, pp. 167–170.