186. *Studies in Chemisorption on Charcoal. Part XI. Some Electrokinetic Properties of Activated Charcoal.*

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Although much work has been published on adsorption by charcoal, little information is available as to the fundamental changes in the electrical condition of the surface, which take place on activation under various conditions. As a result of extensive preliminary work, a standard technique has been developed for obtaining reproducible measurements of the cataphoretic migration velocity of charcoal suspensions by a method using the principle of the ultramicroscope.

It is found that equilibrium conditions are set up after 4—5 hours' activation at a given temperature, and that the cataphoretic velocity varies in the same way as adsorptive capacity. Oxygen-activated charcoal is always negatively charged in pure water, there being a pronounced maximum with samples activated at *ca.* 850°. The effect of the concentration of the charcoal suspension on cataphoretic velocity is also studied.

IMPROVED technique has made electrokinetic measurement one of the most successful methods of investigating the solid–liquid interface. The charcoal surface, one of the most important for practical purposes, has attracted little attention in this field, the position being stated by Abramson (" Electrokinetic Phenomena," 1934, p. 221) as follows : " While thousands of papers have been published describing the adsorptive properties of charcoal, very little is known in regard to the fundamental changes in surface properties as determined by electrokinetic measurement."

A certain amount of work has, indeed, been done on electro-osmosis through carbon membranes or filters, Perrin (*J. Chim. physique*, 1904, **2**, 601) noting that traces of electrolytes had an appreciable effect on the charge and, further, that powdered carbon became positively charged in slightly acid water and negatively charged in water rendered feebly alkaline. Although Perrin's work was confined to electro-osmosis, he realised fully that the cataphoresis of suspended charcoal particles in dilute electrolyte was the converse process and that the same general principles were involved. Similar investigations were carried out by Gyemant (*Kolloid-Z.*, 1921, **28**, 103) and by Umetsu (*Biochem. Z.*, 1923, **135**, 442) who used this as a method of determining the isoelectric point and found that charcoals were positive in both acid and alkaline media. Ogawa (*ibid.*, 1925, **161**, 275) extended the work to the investigation of charcoals activated by various means, and concluded that electrical as well as adsorptive properties were changed by reason of the activation.

The earliest work on the cataphoresis of suspended charcoal particles seems to be due to Goldberg (*Kolloid-Z.*, 1922, **30**, 230) who, using colloidal carbon prepared by the method of Sabbatani (*ibid.*, 1914, **14**, 29), made extensive observations on the influence of various factors on the cataphoretic velocity. The colloidal suspension, obtained by the action of sulphuric acid on sugar, followed by dialysis, was very stable and the particles were negatively charged in both acid and alkaline solution. Migration velocities varied from 13·5 to 18·3μ/sec. per volt/cm., both dilution and filtration causing an increase to a maximum value (cf. p. 994). Acids and bases caused a velocity decrease, and among soluble salts, only those of aluminium seemed to have an appreciable effect, resulting in a velocity increase to a maximum, followed by a decrease on the addition of more salt. Fromageot (*Compt. rend.*, 1924, **179**, 1404) found that the cataphoretic velocity of charcoal particles in solutions of organic acids and their sodium salts depended only on the hydrogen-ion concentration, decreasing as the latter increased. The velocity was unaffected by the extent to which the acid or salt was adsorbed. Hence it was inferred that the acids were adsorbed as undissociated molecules directly on the carbon surface and not through the medium of the double layer. More recent work of Frampton and Gortner (*J. Physical Chem.*, 1936, **41**, 567) tends to confirm this.

Kruyt and de Kadt (*Kolloid-Z.*, 1929, **47**, 44), using ash-free charcoal, showed both by cataphoresis and by electrolyte coagulation that the particles of charcoal are negatively charged in water. Charcoal heated in a vacuum or at 1000° in carbon dioxide became positively charged in water, and it was possible to restore the negative charge by heating to 400° in oxygen. We and others have been unable to obtain positively charged charcoal by this means. Kruyt and de Kadt found further (*Kolloid Beih.*, 1931, **32**, 249) that the high-temperature " positive " charcoal would not adsorb alkali (sodium hydroxide), although the negative sample had a great affinity for it. In this connexion, therefore, it is interesting that we have shown that charcoal heated to a high temperature (*ca.* 850°) is negative although base excluding. It was further suggested by Kruyt and de Kadt that by treatment of charcoal at 400° a surface compound was obtained which gave carboxyl groups with water, but that this compound is decomposed at 1000° leaving a positive surface of carbon. Pilojan and his collaborators (*Kolloid-Z.*, 1933, **64**, 287), studying both platinised and unplatinised charcoal, showed that charcoal is negatively charged after activation at 400° for 15 hrs., but that this charge is reversed by lanthanum or thorium ions.

It is now generally recognised that the surface of charcoal is covered with a chemically adsorbed film of oxygen, the nature of which conditions the properties of the adsorbent. During the last few years, evidence has accumulated which indicates that the nature of this layer of surface oxide varies with the temperature of its formation, and with it, the

adsorptive and catalytic properties of the charcoal (J., 1935, 889; 1936, 1688; 1937, 1489). It thus seemed desirable that a systematic study of the electrokinetic properties of the charcoal surface should be made, particularly in respect to the temperature of activation. Since the inception of the present work, two papers on the subject have appeared. In the first, Olin, Lykins, and Munro (*Ind. Eng. Chem.*, 1935, **27**, 690) attempt to correlate intrinsic adsorptive capacity with electrokinetic behaviour and find, as a result of a series of experiments on peat charcoal, that the two properties are parallel. " The inherent quality which makes a charcoal highly adsorptive," they conclude, " enables it to rob ions of their charges and build up thereby a high ζ-potential, as observed by measurements of cataphoretic velocity of the suspended charcoals." In the second paper, Frampton and Gortner (*loc. cit.*) reach the opposite conclusion, *viz.*, that activation of charcoal does not affect its electrokinetic properties.

<div align="center">EXPERIMENTAL.</div>

Apparatus.—Of the methods available for measurement of cataphoretic velocity, that depending on the use of the ultramicroscope principle was found to be the most suitable for the present work. The technique of Mattson and Mooney (*J. Physical Chem.*, 1928, **32**, 1532; 1933, **37**, 223; *Physical Rev.*, 1924, **23**, 396), which involves observations of the motion of particles suspended in liquid in a cylindrical cataphoresis cell, was therefore adopted. The cell (Fig. 1), of Pyrex glass, consisted of a thick-walled tube 22 cm. long and of 2·0—2·5 mm. internal diameter, joined at each end to wider tubing (*B, C*). At *D* the glass was ground down to within 0·25 mm. of the inner wall, and at right angles to this, another surface was ground, as wide as the bore of the tube; both surfaces were well polished. Large platinum electrodes *E* were sealed in, as near to the entrances of the narrow tube as possible. The cell was then clipped to a wooden holder, and this in turn was fixed rigidly to the microscope stage.

FIG. 1.
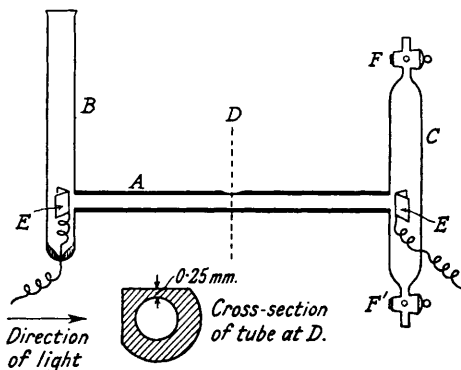
The cell was filled through the stopcock *F* and emptied through *F'*. These stopcocks were tested to ensure that there was no leakage, however slight, to interfere with the flow in the closed tube. This arrangement enabled rapid and efficient washing to be carried out.

The particles in suspension in the cataphoresis tube were illuminated on the principle of the ultramicroscope, the source of light being a high-power electric lamp. The light, after passing through a condenser lens and a heat absorber of alum solution, was brought to a focus inside the cataphoresis tube (at *D*), directly under the microscope, by means of a low-power microscope objective. This objective was fixed to a movable metal arm attached to a vernier scale, and could be moved up and down by means of a screw. This enabled measurements of particle velocity to be made at different levels in the tube; since the tube was closed, the velocity varied greatly from the walls to the centre. Under these conditions of illumination, the particles of charcoal appear as long, scintillating lines against a dark ground.

The eye-piece of the microscope was fitted with four cross wires, making a central square. Particles were spotted just outside one wire and timed with a stop-watch reading to 0·1 sec. across the square to the other wire, the distance travelled being 60 μ. The current, 220 v. *D.C.*, was then reversed, and the observations repeated in the opposite direction. Owing to Brownian movement and consequent disappearance of some particles, it was not always possible to follow a particle right across the square, especially when the time taken was greater than 10 secs. However, by making 5—10 similar observations in each direction, a repeatable average velocity could be obtained. The potential gradient in the tube was occasionally checked by an electrostatic voltmeter.

The level at which the particles were observed was governed by the usual conditions of flow in a closed tube, there being electro-osmotic flow of the water near the walls of the tube towards the cathode, and in the opposite direction at the centre. There must therefore be an annular space within the tube where water velocity is nil and where the true cataphoretic migration velocity of the particles can be observed. According to Smoluchowski (Abramson,

op. cit., p. 76), the distance of this annular space from the axis of the tube is 0·707r, where r is the radius. This, then, determined the level at which the light was focused and at which all measurements were made.*

Activation of Charcoal.—The charcoal was prepared from " AnalaR " sucrose, and activated as described in the previous paper (this vol., p. 691).

Suspension of the Charcoal.—Suspensions of known weights of charcoal were made in clean, steamed-out test-tubes, fitted with tin-foil-covered corks. The distilled water used was re-distilled immediately before use, from a Pyrex flask fitted with a long Pyrex still-head containing glass beads and tubing. Weighed quantities of charcoal were tipped into the dry tube, and 25 c.c. of distilled water poured in. It was then corked and well shaken, after which the heavier particles were allowed to settle, conveniently, overnight. When the charcoal had previously been ground in an agate mortar, it was found that the many heavier particles had settled, so the " clear " supernatant liquid was then decanted into the clean cataphoresis cell for immediate examination. It is of interest that this sharp separation was not always obtained, since there sometimes appeared to be a definite banding in the sedimentation. This was characterised by levels of higher concentration (shown by darkness of suspension) of particles, separated by distances which, as nearly as could be ascertained, were connected in somewhat the same manner as the familiar Liesegang rings.

In the determinations of the velocity–time of activation relationship, activation was periodic-

FIG. 2.
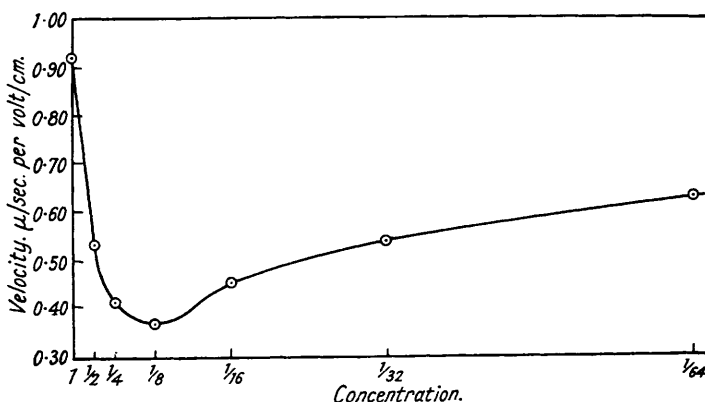
ally interrupted for the removal of a small sample of the charcoal. This was rapidly cooled and ground in the agate mortar for gradually decreasing times (to allow for the progressive breaking up which accompanies activation), 0·1-g. samples then being weighed out and the usual procedure (see above) repeated. This sampling process was continued until no appreciable change in the cataphoretic velocity was observed in successive samples. Simultaneously, an iodine check on a number of activations was carried out, 0·5 g. of charcoal being added to 50 c.c. of standard (*ca.* N/10) iodine, and the adsorption measured after equilibrium had been attained. It was assumed that in the case of identical samples activated at a given temperature, variations in both iodine adsorption and cataphoretic velocity were due, after the initial period at any rate, to change in *surface area* and consequent alterations in the adsorption equilibrium.

Effect of Time of Passage of Uni-directional Continuous Current.—The cell was filled with a fine suspension, the current (220 v. *D.C.*) switched on, and the cataphoretic velocity of the charcoal particles observed at hourly intervals. The time of passage between the wires gradually lengthened from 5·0 to 14·3 secs. during 8 hours of continuous flow. This is presumably due to accumulation of electrolysis products such as disturb also the moving-boundary method. Clearly this effect could be avoided by making the observations over small intervals and reversing the current periodically.

Effect of Dilution of the Suspension.—(i) *Direct dilution.* A sample of charcoal was activated

* Dr. D. C. Henry has kindly pointed out to us (see following paper) that, owing to a neglect in considering the optical properties of the cell, which is in fact a cylindrical plano-concave lens, the point of focus in the present work was actually at a level of approximately 0·76r instead of 0·707r from the axis. This means that the absolute velocity of the charcoal particles is about 5μ/sec. per volt/cm. less than the values quoted. As this correction is constant, it does not alter the shapes of the curves.

for 6 hours at 450°. 0·30 G. was suspended in 50 c.c. of distilled water, the suspension divided into two parts, and separate measurements of the velocity made from each half in order to ensure that the apparatus was giving identical results for identical samples. The results were always reproducible to within 1%. One sample was then diluted to 50 c.c. with distilled water, and the new velocity taken; it had appreciably diminished. This process of dilution was further continued until with 1/64th concentration little further change in the cataphoretic velocity was observed with successive samples. The results, plotted in Fig. 2, are chiefly remarkable for the minimum velocity at 1/8th concentration; the final value never reached that of the undiluted sample.

(ii) *Variation of weight of charcoal in the suspension.* In this series of experiments, the volume of the suspension was maintained at 25 c.c., but different weights of charcoal were weighed into it. The usual procedure of measurement was adopted with the following results :

Wt. of ground charcoal (g.)	0·07	0·11	0·16	0·23
Time of passage (secs.)	10·4	10·3	9·7	9·1

It will be noted that an appreciable change was observed only when the mass of charcoal was more than doubled.

(iii) *Variation due to grinding.* A sample of charcoal was divided into two roughly equal parts, which were then ground in the agate mortar for 4 and 8 minutes severally. The cata-

FIG. 3.
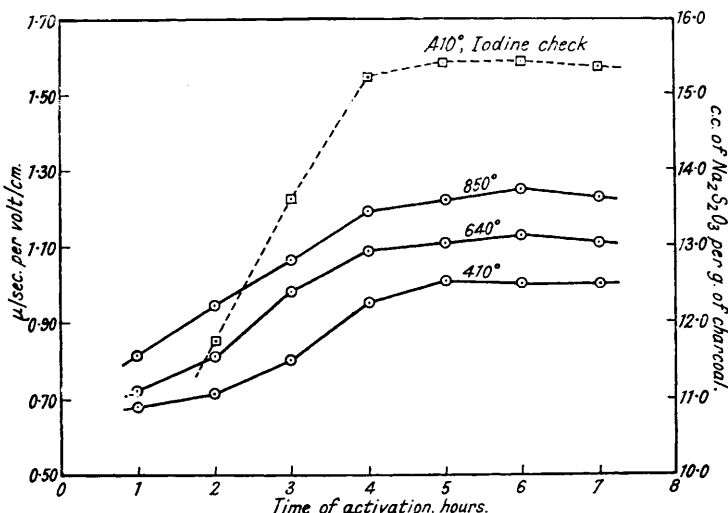
phoretic velocities were measured after both samples had been allowed to settle for the same period of time, with the following results :

	4 Mins.' grinding.				8 Mins.' grinding.			
Wt. of charcoal (g.)	0·07	0·11	0·16	0·23	0·075	0·11	0·165	0·22
Time of passage (secs.)	10·4	10·3	9·7	9·1	8·8	8·9	8·2	7·9

The variation here is clearly due to a greater amount of charcoal remaining in suspension in the latter case, owing to smaller particle size (see also Henry, *Proc. Roy. Soc.*, 1931, *A*, **135**, 124).

Time of Activation, and Cataphoretic Velocity.—As the main object of the present research was to obtain information as to the variation of cataphoretic velocity with temperature of activation, it was important that activation should be sufficiently prolonged so that surface equilibrium might be established, and with it, constant electrokinetic behaviour. A series of activations was therefore carried out at representative temperatures, 410°, 640°, and 850°, samples being withdrawn at hourly intervals and the cataphoretic velocity determined. In the case of the 410° charcoal, iodine adsorption was also measured with samples withdrawn every hour during the activation. The results are plotted in Fig. 3.

It is readily seen that after 4—5 hours' activation, a steady electrokinetic state of the surface is reached, and that after that time the cataphoretic velocity is characteristic of the temperature of activation. The iodine adsorption curve is similar in form to that of the cataphoresis,

steady conditions also being reached in 4—5 hours. These results recall the work of Olin and his co-workers (*loc. cit.*), who also showed that there exists a distinct parallel between intrinsic adsorptive capacity and electrokinetic behaviour.

Conclusions from Preliminary Work.—As a result of the foregoing, the following conditions have to be considered if significant results are to be obtained. The values in parentheses represent the standards adopted : (*a*) Standard grinding (1 minute). (*b*) Standard concentration of the suspension (0·1 g. in 25 c.c. of water). (*c*) Standard suspension procedure (suspensions left to settle overnight). (*d*) Time of examination under a potential difference to be a minimum (10—15 mins.; current was reversed after each individual measurement lasting a few seconds).

RESULTS AND DISCUSSION.

Samples of pure sugar charcoal were activated at a number of temperatures varying from 380° to 1030°, and the cataphoretic velocity of the products measured by the standard procedure given above. It was found that charcoals activated at temperatures higher than 550° moved with a considerable velocity, the time of passage of the particles across the field

FIG. 4.
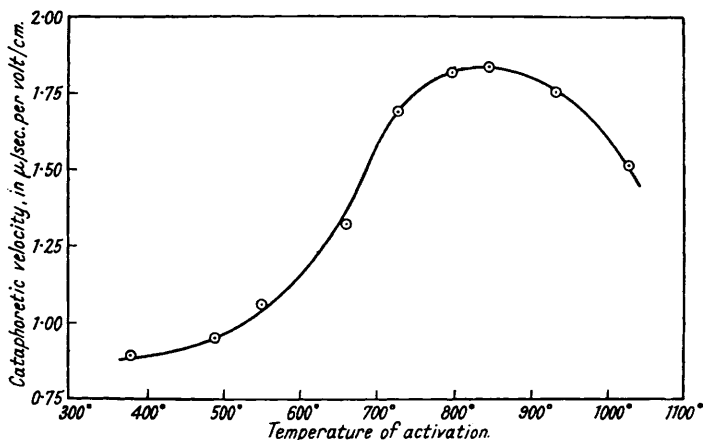
of view being in some instances less than 3·3 secs. All observations were therefore repeated with a potential difference of 110 v. instead of 220 v., enabling more accurate results to be obtained. The results of the two series of measurements agreed; they are plotted in Fig. 4.

It will be seen from the curve that, as the activation temperature is increased from 380° to 850°, there is a gradual increase in the cataphoretic velocity of the suspended charcoal in pure water ($p_H = 6·9$). Between 800° and 850° a definite maximum is obtained, and with further increase in the temperature of activation, the velocity falls rapidly. This is in agreement with, and is an extension of, the work of Olin (*loc. cit.*) on peat charcoal.

The maximum at 800—850° may be correlated with several other phenomena on the charcoal surface. For instance, it is well known that maximum acid adsorption and minimum base adsorption occur with charcoals activated at 800—850°, while the maximum efficiency as an oxidising catalyst and minimum efficiency in the decomposition of hydrogen peroxide are also exhibited by samples activated at that temperature. In addition, 800—850° is the range of maximum hydrolytic adsorption (see p. 691) and of p_H value of charcoal suspensions. In order to explain these and other phenomena, the existence of surface oxides of carbon of different chemical constitution has been invoked. For instance, Frumkin (*Z. physikal. Chem.*, 1929, *A*, **141**, 141) suggested that, in the case of a charcoal activated at a high temperature, the following reaction took place in aqueous suspension : $C_xO + H_2O = C_x^{++} + 2OH^-$, *i.e.*, the charcoal particles acquire a positive charge with respect to the medium. The idea that high-temperature charcoals are positive is prevalent in the literature, and the results of Kruyt and de Kadt (*loc. cit.*) on this point have been much quoted. It is interesting to note, therefore, that the present authors have found

no evidence for the existence of a positive charcoal; indeed, a sample of charcoal activated at 850° and suspended in pure water has an extraordinarily high negative velocity, much greater, in fact, than that of a 450° sample which, by widespread confirmation, is definitely negative. Within the range of activation temperatures here employed, no charcoal was found which was isoelectric in pure water, yet a 500° sample (p. 691 *et seq.*) adsorbs acids and bases to an equal extent. No correlation between charge and surface constitution will be attempted at this stage.

Throughout the range of temperatures used, the variation in velocity from temperature to temperature is more than 100%, and the procedure adopted in activation and suspending has been carefully standardised as a result of extensive preliminary work. It is therefore somewhat surprising that Frampton and Gortner (*loc. cit.*) find that " activation does not affect the electrokinetic properties, since the migration velocity of various charcoals suspended in water is remarkably constant." The values quoted in support of this are indeed constant, yet no standard method or time of activation was adopted : the time varied from 2 to as much as 24 hours. In addition, Frampton and Gortner appear to have varied the treatment of the charcoal with liquids and gases, conditions which were constant in the present work.

The effect of dilution of the suspended charcoal on the cataphoretic velocity (Fig. 2) is of interest. The shape of the curve recalls the work of von Buzagh (*Kolloid-Z.*, 1927, **41**, 169; 1928, **46**, 178) on the disperse-phase rule, since it appears that, for a medium concentration of charcoal suspension, the cataphoretic velocity is a minimum, increasing for both higher and lower dilutions. Actually, von Buzagh (*ibid.*, 1928, **48**, 33) carried out some interesting experiments on the cataphoresis of animal charcoal suspended in picric acid solution, and found maxima in the curves connecting cataphoretic velocity with concentration of both solid phase and electrolyte when each was varied independently. He assumed, therefore, that there was a definite charge on the particles necessary for peptisation, and that it was related to a definite adsorbed amount of peptising agent. Thus, for small amounts of solid phase, the electrolyte concentration was too high to permit high migration velocity, while for large amounts it was too low and thus unable to stabilise the particles. For medium concentrations, maximum electrokinetic properties were exhibited. Von Buzagh nevertheless states that in pure water the velocity is independent of the amount of solid phase, the degree of peptisation for small amounts being constant.

It would seem that, in the present instance, the charcoal activated at 450°, and therefore negative when suspended in water, undergoes two opposing processes on dilution, the first resulting in a diminution of negative charge and the second, taking effect after much dilution, restoring the balance to some degree. Mukherjee (*Kolloid. Beih.*, 1936, **43**, 417) and Lottermoser and Chang (*Kolloid Z.*, 1933, **64**, 268) have noticed a similar effect with ferric oxide sols, and suggest that dissociation of the colloidal electrolyte occurs simultaneously with transference of negative (Cl^-) ions from suspended particles to suspension medium; in charcoal, adsorption and dissociation are the probable causes of the minimum.