355. *Studies in Chemisorption on Charcoal. Part XII. The Isoelectric Point.*

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The cataphoretic migration velocities of charcoals activated in moist oxygen at different temperatures and suspended in solutions of hydrochloric acid and of sodium hydroxide of various p_H have been measured by means of the ultramicroscope method. It is found that in these solutions all the charcoals are isoelectric between p_H 3·0 and 4·0, and that there is an approach to a second isoelectric point in the neighbourhood of p_H 1·0—1·5. The effect of the temperature of activation is marked in solutions of p_H greater than 4·0, those activated at 850° having a maximum negative velocity. All the charcoals examined were negatively charged in all solutions of p_H 4·0 and above.

SEVERAL workers, including Hauge and Williman (*Ind. Eng. Chem.*, 1927, **19**, 942), have pointed out that the adsorption of dissolved materials by carbon varies with the p_H of the solution or that the effectiveness of the adsorbent depends on the potential difference between the carbon and the adsorbate. For instance, with increasing hydroxyl-ion concentration, charcoal becomes progressively more negative and then tends to adsorb positively charged particles; in acid media the opposite is the case. It is important, therefore, to know the isoelectric point of an adsorbent and to have information as to its electrokinetic behaviour in acid and in alkaline solutions.

In Part XI (this vol., p. 991) we discussed the electrokinetic properties of pure charcoals activated at different temperatures and suspended in pure water. This work is here extended to observations of similar charcoals in acid and alkaline solutions.

Several attempts have been made to measure the isoelectric point of charcoal by various methods. Umetsu (*Biochem. Z.*, 1923, **135**, 442), studying electro-osmosis through filters of blood charcoal, found an isoelectric point at p_H 3·0, but noted that sugar charcoal was positive throughout the p_H range studied. Bovic (*J. Med. Res.*, 1915, **33**, 295) reported vaguely as to the buffer action of charcoal, and many other investigators have shown that acid solutions become less acid, and alkaline solutions less alkaline, on treatment with charcoal. Gyemant (*Kolloid Z.*, 1921, **28**, 103) found animal charcoal to be isoelectric at p_H 4·0, although Loeffler and Spiro (*Helv. Chim. Acta*, 1919, **2**, 417), using citrate, phosphate, and borate buffers, were unable to assign a definite p_H to the isoelectric point. Later, Bohn (*Biochem. Z.*, 1926, **178**, 119) reported that he was unable to assign a definite isoelectric point to all charcoals, variations being due to changing buffer capacity of the solutions and to impurities. He showed, in particular, that the change caused by a particular sample of charcoal depended on the amount of buffer solution, its buffer capacity, and the difference between the p_H of the solution and the isoelectric point of the adsorbent. His results showed, as did those of Spengler and Landt (*Z. ver. deut. Zucker-Ind.*, 1928, **78**, 81), a variation in isoelectric point from p_H 5·0 to 8·9. This chaotic state of affairs is illustrated by Table I, where determinations of the isoelectric point of charcoals by various authors are collected.

TABLE I.

Author.	Date.	Type of charcoal.	Isoelectric point (p_H units).
Umetsu	1923	Blood	3·0
Gyemant	1921	Animal	4·0
Krczil *	1931	Blood	3·5
Spengler and Landt	1928	Various	5·0—9·0
Bohn	1926	Standard norit	8·6
		Superior norit	5·9—7·7
		Eponit special	8·7
		Carboraffin	5·9
Krczil *	1931	Beechwood (Kahlbaum)	6·6
		Animal (Merck)	4·0
		Carbovent	3·9
Olin, Lykins, and Munro	1935	U.S.A. Bureau of Standards coconut charcoal	2·4
Present authors	1938	Pure sugar charcoals	3·0—4·0

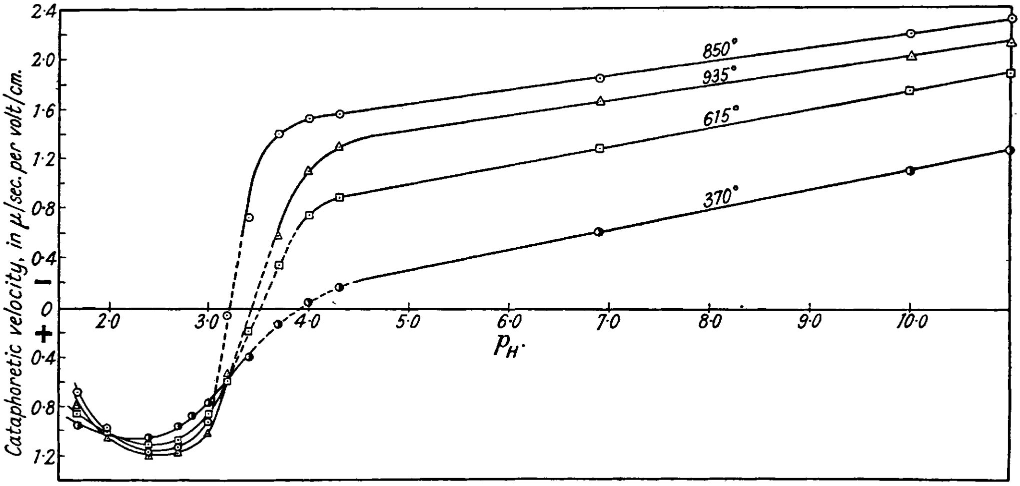
* " Untersuchung und Bewertung technische Adsorptionsstoffe," Leipzig, 1931, pp. 121, 125.

In 1927, Miller and Bandemer (" Colloid Symposium Monograph," p. 76) disputed the very existence of the isoelectric point of charcoal. The contention was, apparently, that as adsorption from buffer solutions is essentially that of acid salt or alkaline salt mixtures, it could be assumed that pure charcoal would not reduce the alkalinity of alkaline buffers. This was based on earlier work of Miller, who had shown that pure charcoal will not adsorb alkali; this now seems doubtful, as it has been proved (King, J., 1937, 1489) that the adsorptive properties of pure charcoals depend on the temperature of activation, those activated or reactivated at low temperatures adsorbing bases, whereas those activated at high temperatures exclude bases. According to Miller, both pure charcoals and blood charcoal, from which the impurities have been removed by volatilisation, show only a buffering action due to adsorption of acids, *i.e.*, there can be no isoelectric point for either pure or blood charcoal; but no results are quoted in support of this contention. Olin, Lykins, and Munro (*Ind. Eng. Chem.*, 1935, **27**, 690), from their work on the cataphoresis of particles of coconut charcoal, concluded that between p_H 1·5 and 5·0 charcoal has two isoelectric points.

In the present work, the cataphoretic velocity has been measured for a series of pure charcoals activated in moist oxygen at different temperatures and suspended in aqueous solutions of various p_H. The results are plotted in the figure.

It is immediately obvious that, in contradiction to Miller's statement that charcoal has no isoelectric point, the material is isoelectric between p_H 3·0 and 4·0. Moreover, in spite of variations in the temperature of activation from 370° to 935° which have a profound effect on the adsorptive and other surface properties of charcoal, the velocity–p_H curve crosses the p_H axis certainly within a range of 1·0 p_H unit in every instance. The actual value of the isoelectric point is best obtained by interpolation, since with solutions of p_H 3·0—4·0, both positive and negative cataphoretic velocities were often too slow to permit of very accurate observation (see p. 1891). In a number of cases, however, intermediate points were obtained within this range by careful choice of particle and diligent observation; these tend to confirm the interpolated parts of the curves.

These curves, with the possible exception of that for the 370° activation, exhibit a marked change in direction at about p_H 4·0, the velocity in each case falling rapidly to zero. The portions below p_H 4·0, however, are smooth and show a maximum positive velocity at about p_H 2·5; thereafter the velocity falls again towards zero and there is a tendency for the p_H axis to be crossed again below p_H 1·5. As far as could be ascertained, therefore, the claim made by Olin and his co-workers (*loc. cit.*) for a dual isoelectric point is substantiated by our results, although we were never actually able to obtain the second point owing to the incidence of electrolysis below p_H 1·7. Nevertheless, the general shape of the curves would seem to indicate approach to isoelectric conditions below p_H 1·5, although the possibility of asymptotic approach to the axis cannot be excluded.



We find also that the 850° specimen, showing the steepest fall in the velocity–p_H curve at 4·0, retains its high negative charge in a similar manner to the coconut charcoal investigated by Olin. The essential difference between the two samples apparently lies in their isoelectric points, our 3·2 corresponding to their 2·4.

The effect of temperature of activation indicates, as does our previous work on aqueous suspensions (Part XI, *loc. cit.*), that the charcoal activated at 850° shows maximum negative charge throughout the whole of the p_H range above the isoelectric point, but it is surprising that charcoals activated at both high and low temperatures and possessing, therefore, contrasting properties, should all be isoelectric between p_H 3·0 and 4·0.

EXPERIMENTAL.

The measurement of cataphoretic migration velocity and the preparation and activation of the charcoal were carried out as already described (Part XI, *loc. cit.*).

At first, attempts were made to measure the velocities in standard buffer solutions, but it was found that the concentrations of electrolytes present in these solutions, even when only 0·1M, were sufficiently great to cause complete discharge of the particles; *e.g.*, a charcoal suspended in pure water had a velocity of 1·5μ/sec. per volt/cm. but was immobilised when suspended in a phosphate–citric acid buffer, irrespective of its p_H. It was then decided to rely on standard solutions of hydrochloric acid and sodium hydroxide, carefully checked at the moment of use by a glass electrode in conjunction with a valve potentiometer. In preliminary observations made with 1-g. samples of charcoals suspended in equal volumes of hydrochloric acid of concentration varying from 0·0001N to 0·02N, it was found that in all cases the mobility of the particles was characteristic and reproducible. At concentrations of the acid greater than 0·02N, electrolysis was noted, whatever the voltage applied across the ends of the cell, and this disturbed the motion of the particles. The following procedure was then adopted. A standard weight of charcoal activated at a given temperature was placed in each of a series of specially cleaned test-tubes, and 25 c.c. of solutions of various p_H were run in. The tubes were then closed with tinfoil-covered corks and shaken, after which the larger particles were allowed to settle out. In the meantime the p_H of the supension medium was determined by the glass-electrode method, so quickly as to be complete before the heavier particles of charcoal had settled in the tubes. The " clear " charcoal suspensions were then decanted into the cataphoresis cell, and the velocity of the actual particles measured in the field of view of the ultramicroscope. The p_H range 1·3—4·3 was obtained by means of hydrochloric acid solutions, readings at 6·9 were taken in redistilled water, and for the two series of high p_H readings (10·0 and 11·0) sodium hydroxide solutions were used. Details of the observations in one case are given in Table II, Henry's correction (this vol., p. 997) for the level in the Mattson cell having been applied. Here the isoelectric point certainly lies between p_H 3·4 and 3·7.

TABLE II.

Temperature of activation, 730°.

p_H of suspension medium	1·7	2·0	2·4	2·7	3·0	3·4	3·7	4·0	4·3	6·9	10·0	11·0
Sign of charge on particles	+	+	+	+	+	+	−	−	−	−	−	−
Velocity, μ/sec. per volt/cm.	0·93	1·05	1·14	1·08	0·93	0·20	0·42	0·88	1·06	1·53	1·93	2·03

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