CCXXVII.—*The Adsorption of Fumaric and Maleic Acids by Pure Charcoals.*

By HAROLD JOHN PHELPS.

IN a recent investigation (Phelps and Peters, *Proc. Roy. Soc.*, 1929, *A*, **124**, 554) it was shown that the adsorption of succinic, propionic, or hexoic acid at different hydrogen-ion concentrations is roughly proportional to the amount of un-ionised acid present, as calculated from the accepted values of the dissociation constants. It was concluded, therefore, that the adsorption proceeded predominantly through the medium of un-ionised molecules. There was, however, no evidence that this statement is strictly true for dibasic acids. The results obtained with succinic acid showed that the adsorption did not become zero until such a hydrogen-ion concentration was reached as corresponded with the complete ionisation of both carboxyl groups. The dissociation constants of succinic acid are, however, too nearly the same for us to generalise as to the behaviour of dibasic acids of which the two constants are widely different.

Further confirmation of these results has been sought in the study of the effect of hydrogen-ion concentration upon the adsorption of fumaric and maleic acids, since these should show characteristic differences if the adsorption were determined by the electrical state of the particles concerned. The dissociation constants of maleic and fumaric acids respectively are given in the literature as $K\alpha_1 = 1{\cdot}17 \times 10^{-2}$ and $9{\cdot}3 \times 10^{-4}$ (Ostwald, *Z. physikal. Chem.*, 1889, **3**, 694), and $K\alpha_2 = 2{\cdot}0 \times 10^{-7}$ and $1{\cdot}18 \times 10^{-5}$ (Chandler, *J. Amer. Chem. Soc.*, 1908, **30**, 170). Thus it will be seen that one of the carboxyl groups of maleic acid is relatively strongly acid while the other is very weak: three possibilities therefore arise with this acid. (1) If the anion produced by the primary ionisation is not adsorbed, the adsorption should fall rapidly in solutions more alkaline than, say, p_H 2·5. (2) If, on the other hand, only the doubly ionised molecule escapes adsorption, then the adsorption should fall off between p_H 5·5 and 7·5 approximately. (3) If the singly ionised molecule is adsorbed to a less degree than the neutral molecule, and the doubly ionised molecule is not adsorbed at all, then the adsorption should fall more or less gradually from p_H 1·5 to p_H 7. The results to be described indicate that the third of these possibilities represents the truth.

The dissociation constants of fumaric acid are so similar that one would expect its adsorption to be affected by hydrogen-ion concentration in almost the same way as that of a monobasic acid.

The results obtained suggest that possibility (2) is the most probable, *i.e.*, only the doubly ionised molecule escapes adsorption.

EXPERIMENTAL.

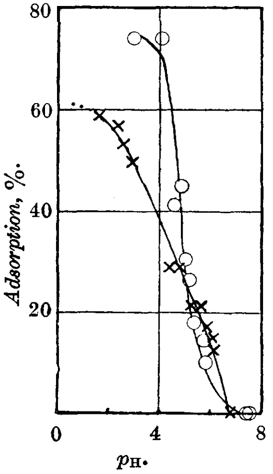
The general technique of the adsorption experiments was identical with that previously employed. 20-C.c. samples of 0·2% solutions of the acids together with suitable small volumes of sulphuric acid or sodium hydroxide were made up in every case to 22 c.c. and shaken with 200 mg. of charcoal, which, like that used previously, had been purified by Miller's method (*J. Physical Chem.*, 1926, **30**, 1031).

The samples of fumaric acid (m. p. 286°) and maleic acid (m. p. 131°) used were obtained from the British Drug Houses, Ltd.

Fumaric and maleic acids were estimated by the method of partial titration, which depends on the fact that the total acid titratable over a region not greatly removed from neutrality is almost wholly weak acid even in presence of relatively large amounts of strong acid (van Slyke and Palmer, *J. Biol. Chem.*, 1920, **41**, 567; Harris, *Proc. Roy. Soc.*, 1924, *B*, **95**, 440). This method had been used for the estimation of propionic and hexoic acids (see above), and in these cases practically all the acid could be accounted for by the titratable acidity between the colour changes of bromophenol-blue and thymolphthalein. In the cases of fumaric and maleic acids, however, only a part of the total acid was found by titration between these limits. The percentage decrement in this amount was taken as a measure of the adsorption that had taken place. This value was open to error from two sources. (1) It is the sum or difference (according to the initial p_H) of two titration values each of which is open to the normal errors of observation; these errors were shown to be not greater than 2% of the total amount of acid present in the solutions originally, and thus make the values of the percentage adsorption liable to this degree of error as a maximum. (2) The acid titratable between the limits specified may be influenced by the amount of sodium salt present, with the result that the titres of solutions of different initial hydrogen-ion concentration may not be strictly comparable; experiment showed, however, that this was not the case, for a series of titrations of maleic acid solutions which had been neutralised to varying extents and which covered the whole range studied (with the exception of one experiment at p_H 1·5) showed no greater deviation than 3%. In the more acid experiments, a third source of observational error is introduced, since a correction must be made for the residual strong acid titrated between p_H 4 and 11. Only in the most acid solutions was this correction found to be necessary.

Results.—The results of the adsorption experiments are shown in the two curves in Fig. 1, which represent the adsorption of fumaric acid (circles) and maleic acid (crosses) plotted against $p_{\rm H}$. As the two acids were used in solutions of similar concentrations (the actual strengths were maleic acid 0·035*N*, and fumaric acid 0·029*N*), the adsorptions are given as percentages of the amount originally present in order to make the two curves as comparable as possible. It will be seen that the adsorption of maleic acid, which is nil in solutions more alkaline than $p_{\rm H}$ 7, rises steadily with increasing hydrogen-ion concentration up to $p_{\rm H}$ 1·5, the most acid solutions with which it was possible to work. The adsorption of fumaric rises from nil at about $p_{\rm H}$ 7 to become maximal at about $p_{\rm H}$ 3·7.

FIG. 1.



Discussion.

The hydrogen-ion concentrations at which the various carboxyl groups of the two acids will be 50% dissociated can be calculated from the values of the dissociation constants given above. They are: for the primary dissociation of maleic acid, $p_{\rm H}$ 1·95, for the secondary dissociation, $p_{\rm H}$ 6·70; for the primary dissociation of fumaric acid, $p_{\rm H}$ 3·03, and for the secondary dissociation, $p_{\rm H}$ 4·75. Thus the adsorption of maleic acid is nil at a $p_{\rm H}$ at which the secondary carboxyl is only 50% dissociated, and has not reached a maximum at a $p_{\rm H}$ at which the primary carboxyl group is 50% dissociated. In the case of fumaric acid, the adsorption has already reached a maximum at a $p_{\rm H}$ at which the primary carboxyl is still 50% dissociated, and is half maximal at a $p_{\rm H}$ at which the secondary carboxyl is half dissociated. The adsorption of maleic is nil, or very low, at a $p_{\rm H}$ at which the secondary carboxyl group is still considerably dissociated, and further, the adsorption is still rising in solutions of such acidity that this group is wholly undissociated.

These results seem consistent with the view that in the case of fumaric acid only the doubly ionised molecule escapes adsorption, while in the case of maleic acid the product of the primary ionisation is absorbed to a less degree than the neutral molecule, and the doubly ionised molecule is scarcely adsorbed at all.

In our previous work (*loc. cit.*) a view was expressed that adsorbed molecules are held at the charcoal surface by chemical or pseudo-chemical valencies of the type postulated by Langmuir. It seems to be a not improbable assumption that the oxygen of the carboxyl group may provide the means by which the carboxylic acids are held at charcoal surfaces. The presence of an un-ionised carboxyl group would thus be necessary for adsorption to take place. In the case of dicarboxylic acids, therefore, the adsorption might be expected to follow the ionisation of the weaker carboxyl group, except in so far as the presence of an electric charge is *per se* an obstacle to adsorption.

Since the accepted formula for maleic acid represents the two carboxyl groups as lying on the same side of the carbon–carbon double link, there is every reason to suppose that the stronger carboxyl group hinders adsorption more on account of its proximity to the weaker un-ionised group than from any other cause. Peters and the author (*loc. cit.*) suggested also that the water sheaths commonly supposed to surround most ions might inhibit their adsorption by purely physical " blocking " which would prevent intimate contact between the ion and any surface it might approach. Although this view is in the highest degree speculative, it may be pointed out that the results here described are consistent with it. In the case of the singly charged maleate ion the weaker un-ionised carboxyl group might be imagined to be " blocked " by the water sheath of the adjacent ionised group.

In conclusion, I would like to express my sincere thanks to Professor Peters, not only for his interest in this work, but also for his continual inspiration in the past.

THE DEPARTMENT OF BIOCHEMISTRY,
OXFORD.

[*Received, May 9th,* 1929.]