DISCONTINUITY OF THE ISOTHERMALS FOR THE ADSORPTION OF PHENOL FROM SOLUTION

BY R. CHAPLIN

In the course of an investigation on an industrial use of active charcoal, which need not be described here, it became necessary to determine at 25° and 60° the adsorption isothermals for a technical active charcoal and phenol in aqueous solution at concentrations lying between 0.1 and 24.0 grams/litre. The results obtained were unusual in that they showed pronounced discontinuity in the relation between quantity of phenol adsorbed and concentration of the solution. In view of suggestions of discontinuity in adsorption processes which have appeared in the literature from time to time,[1] and particularly in view of a recent paper on the subject by Allmand and Burrage,[2] it was felt that these results might be of academic interest.

The charcoal used in the investigation referred to was of the extruded type, activated by the zinc chloride process and had no exceptional properties in any way. The discontinuity observed, therefore, would seem at first sight to be characteristic of the sorbate. But it may be that phenols merely show up in a pronounced way a phenomenon which is characteristic of the adsorption process in general, and this is the real point of interest. Data for other sorbates, obtained under the conditions described below, would be helpful in further elucidating the matter.

A working description of the method used, and the results obtained, are given in what follows.

Experimental Method

The apparatus used consisted simply of a 300 c.c. wide-necked flask fitted with a bung carrying a small glass stirrer and a short, corked tube 1 cm. in diameter, which served for the withdrawal of solution or the introduction of water.

220 c.c. of water at 25°C. or at 60°C. were run into the flask, the requisite weight of pure phenol added and the flask was corked and immersed to the neck in a bath at 25°C. or at 60°C. Stirring was commenced and after the adjustment of temperature 20 c.c. of solution were withdrawn for analysis. The phenol was estimated in the usual way by Koppeschaar's bromination method[3] which was found to give results accurate to within 1% of the phenol present. The bung was then removed and about 2 grams of charcoal, previously dried at 130°C. in a U-tube and weighed therein, were introduced. The bung was quickly replaced and the charcoal and solution were stirred together for 3 hours, after which samples of solution were withdrawn for

[1] Recently N. Semenov: Z. physik. Chem., **1930** B7, 471.

[2] Proc. Roy. Soc., **130** A, 610 (1931).

[3] Z. anal. Chem., **15**, 233 (1876).

analysis. The quantity of phenol adsorbed was calculated from the fall in concentration and the total bulk of solution, and was then referred to unit weight of charcoal and plotted against the final phenol concentration.

For the approximate isothermal given in Table I successive points were obtained by increasing the phenol concentration above that for the preceding point, following the procedure just described, and adding the value for phenol adsorbed to that previously calculated, the total phenol adsorbed at any stage being plotted against the corresponding final concentration. Such a method evidently gives rise to cumulative error and this was found to be very considerable in the present case after the determination of a number of points. The error is mainly due to the slowness with which equilibrium is finally approached in the adsorption of phenol from solution and, in order to avoid it, fresh charcoal was used for each point of the isothermals given in Tables II and III. The use of fresh charcoal for each point conduces to much greater accuracy in work of this kind and tends to reveal the true form of isothermal. The only exceptions to the new procedure are the few desorption points shown by the letter D in Table II (crosses in Fig. 2) which were unavoidably dependent on a prior sorption point. For the determination of these the solution in contact with the charcoal at the conclusion of sorption was diluted with water and the quantity of phenol withdrawn was calculated from the rise in phenol concentration above that corresponding to dilution.

The time of contact adopted was decided on as a result of rough velocity measurements (not given) at 25° and 60°. These showed that after 3 hours the adsorption became comparatively slow and the results could then be sufficiently well reproduced.

Results

TABLE I

60° Phenol Isothermal (approximate values)

A = Phenol Conc., grams/litre

B = Quantity adsorbed, mgrs./gram

A	B	A	B
0.6	140	15.5	365
1.2	165	16.0	410
2.0	185	18.6	410
9.2	200	21.0	410
11.0	200	24.0	453
16.0	215		

The results in Table I are plotted in Fig. 1 (isothermal 1).

ADSORPTION OF PHENOL FROM SOLUTION. ISOTHERMAL

FIG. I
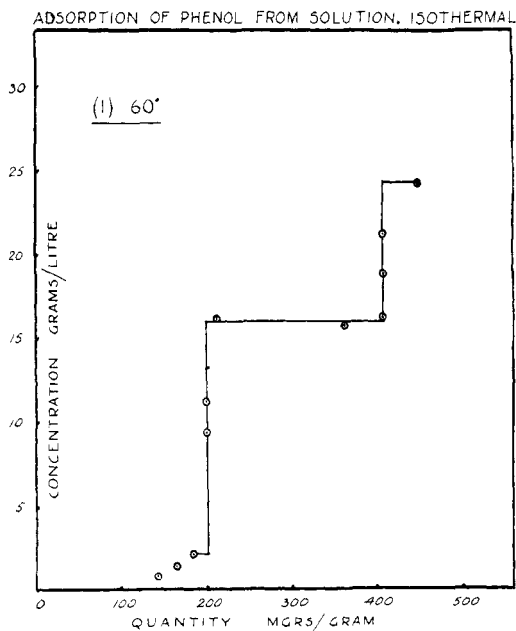
TABLE II

60°C. Phenol Isothermal

A = Phenol Conc., grams/litre

B = Quantity adsorbed, mgrs./gram

A	B	A	B
0.14	52	D 0.64	138
0.22	81	2.06	186
0.33	98	D 1.20	166
0.40	128	3.07	192
D 0.28	128	D 2.39	188
1.04	152		

TABLE III

25°C. Phenol Isothermal

A = Phenol Conc., grams/litre

B = Quantity adsorbed, mgrs./gram

A	B	A	B
0.10	65.5	0.96	151.0
0.24	93.5	1.43	167.5
0.37	120.0	1.45	191.5
0.49	123.0	1.81	187.0
0.68	124.0	2.24	190.0
0.70	136.0	3.00	191.0
0.78	136.0		

ADSORPTION OF PHENOL FROM SOLUTION.   ISOTHERMALS.
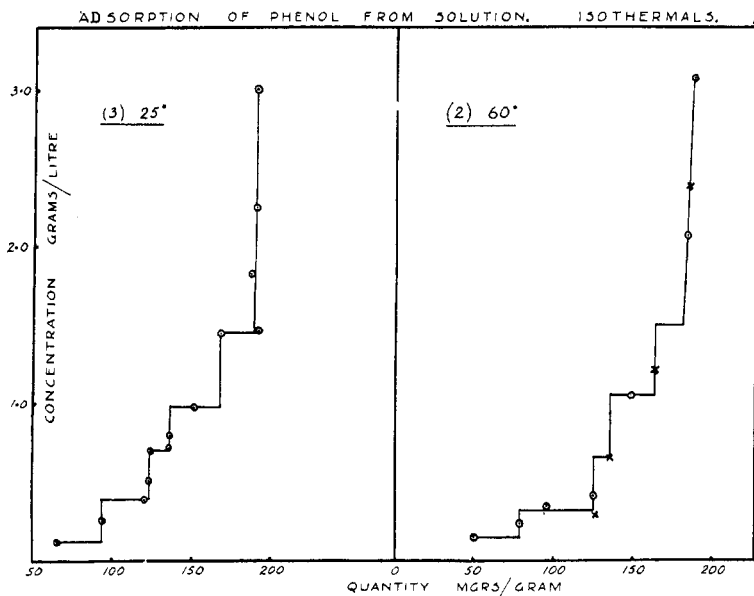
FIG. 2

The results in Tables II and III are plotted in Fig. 2 (isothermals 2 and 3).

Discussion

Isothermal 1 extends up to concentrations some 10 times as high as those of isothermals 2 and 3 but it gives no information as to form at low concentrations. Accordingly in the determination of isothermals 2 and 3 the concentrations have mainly been kept below the value at which isothermal 1 begins and these isothermals have been plotted on a more open scale.

There is perhaps some choice as to how the points may be joined up—particularly the lower terminal points—but taking the three sets of results into consideration the discontinuous nature of the isothermals can hardly be doubted. The most convincing case is isothermal 3 in which several of the experimental points were determined as nearly as possible at the turning point values. The exact form of the isothermals could, of course, only be determined by taking a considerably larger number of points than was here done.

The large increase in phenol content of the charcoal without further increase in concentration of solution which occurs at 16 grams/litre, shown in isothermal 1, recalls the behaviour of charcoal with water vapour at 12–15 m.m. partial pressure.[4]

⁴ Allmand, Chaplin and Shiels: J. Phys. Chem., **33**, 1151; Allmand and Hand: 1161 (1929).