

CXXIII.—*The Sorption of Alcohol and Water by Animal Charcoal.*

By JOHN DRIVER and JAMES BRIERLEY FIRTH.

A CONSIDERABLE amount of data has already been published regarding the sorption of substances in solution by charcoal. In calculating the results, in nearly every case it has been assumed that the solvent is not sorbed, or the amount sorbed is so small that it can be neglected.

One of us has already shown (Firth, *Trans. Faraday Soc.*, 1921, 16, 434) that in the case of the sorption of iodine from solution in organic solvents the nature of the solvent materially affects the rate of sorption, and also that the final equilibrium (which is only attained after a very long period) is to some extent dependent on the solvent. One factor that influenced the sorption was the solubility of the dissolved substance in the liquid solvent.

The sorption of liquids does not appear to have been studied to any great extent and the quantitative data available are comparatively small.

Gurvitsch (*J. Russ. Phys. Chem. Soc.*, 1915, 47, 805) has made a study of the sorption of water and various organic liquids by fuller's earth, bone charcoal, and kaolin, and obtained the following important result—that the volumes of liquid adsorbed vary over a relatively small range from 0.61 to 0.684 c.c. per gram of sorbing substance. He attributes adsorption to physicochemical forces and rejects the view that it is due to purely chemical forces on the following grounds. (1) The amounts of the different liquids adsorbed by a given amount of adsorbent are not in agreement with stoichiometric relations. (2) The range of action of the forces causing adsorption is always of the order 3×10^{-8} cm., whereas

the range of action of the force of chemical affinity is limited to distances of atomic order or, at most, to the distances separating neighbouring molecules. The sphere of action of physicochemical forces is many times greater. (3) The heat of reaction between any two elements is, generally speaking, greater the more dissimilar are the elements. In the action of residual chemical energy (physicochemical force) we see just the reverse: hydrocarbons generate much more heat with charcoal than with fuller's earth or kaolin; alcohols act in the reverse manner.

Langmuir (*J. Amer. Chem. Soc.*, 1917, **39**, 1848), in a criticism of the work of Gurvitsch, rejects the view that sorption is due to physicochemical forces, and states "the forces involved in adsorption are strictly chemical in nature, that is, they do not differ in any essential respect from the forces causing the formation of typical compounds." The absence of stoichiometric relationship can be taken as proof, not of the absence of chemical combination, but that it is simply the result of steric hindrance. The following quotation gives Langmuir's view of the processes occurring during the adsorption of ethyl alcohol by charcoal. "The hydroxyl groups of the alcohol are attracted to the carbon atoms, so that as many carbon atoms as possible come into contact (or combine) with the hydroxyl groups. The ethyl groups fill up many of the small cavities, and, in other ways, prevent the hydroxyl groups from coming into contact with the carbon atoms. The larger pores or cavities are, however, covered over with a single layer of molecules. When the vapour is saturated, it is evident that these cavities must gradually become filled with liquid. But this is to be classed as capillary phenomena and not as adsorption. It has, for example, nothing to do with the forces acting between the carbon atoms and the hydroxyl groups.

"Under these conditions it is only natural that the volume absorbed should be about the same for different liquids, since it is simply a measure of the total volume of the larger pores."

Bakr and King (this vol., p. 454), in a communication published since this work was completed, show that the sorption of benzene from iodine solutions is less than that from the pure solvent. They further show that the effect of neglecting the sorption of the solvent benzene in calculating the sorption of iodine is very small in this case.

The object of the present communication was to study the sorption of water and alcohol by animal charcoal and also the sorptive effect with mixtures of alcohol and water.

EXPERIMENTAL.

The animal charcoal used was Merck's highly purified variety, and it gave 4.435 per cent. of ash. It was digested several times with concentrated hydrochloric acid, washed with water, and finally boiled with distilled water until free from phosphates and chlorides; the ash was then 1.05 per cent. and the density 1.966. The charcoal was very finely powdered. The alcohol was dried for several days over calcium oxide and distilled, then dried with metallic calcium and again distilled, the first and the last portions being rejected. Its density at 25° was 0.78572.

Ordinary distilled water was treated with alkaline potassium permanganate and distilled, the middle portion only being used. This was then twice redistilled; the product gave no appreciable residue on evaporation.

The Determination of the Sorption of (a) Water (b) Alcohol.

The charcoal was heated at a dull red heat in a vacuum for about three hours and then allowed to cool in a vacuum. A quantity of the charcoal was then quickly weighed out into a well-stoppered tube fitted with a leading-tube and tap. About 5 c.c. of distilled water were introduced into a similar tube and the two tubes connected by means of a T-piece, also fitted with a tap. The apparatus was exhausted and placed in a thermostat at 25°. The tube containing the charcoal was carefully disconnected at definite intervals and weighed, until the weight became constant.

A similar series of results was obtained, using alcohol instead of water. The results are given in the following table, where m is the weight of charcoal used and x the c.c. of liquid sorbed.

TABLE I.

Water.			Alcohol.		
$m = 1.0398$ grams.			$m = 1.1272$ grams		
Time. Days.	x	$\frac{x}{m}$	Time. Days.	x	$\frac{x}{m}$
1	0.0118	0.0113	1	0.1464	0.1299
4	0.0210	0.0202	2	0.2753	0.2442
8	0.0298	0.0286	4	0.3469	0.3077
14	0.0408	0.0392	7	0.4147	0.3679
18	0.0480	0.0462	10	0.4867	0.4318
22	0.0553	0.0532	15	0.5596	0.4965
33	0.0732	0.0704	20	0.5963	0.5299
48	0.1094	0.1062	25	0.6292	0.5582
60	0.1394	0.1340	37	0.6894	0.6205
70	0.1398	0.1345	60	0.6894	0.6205
80	0.1397	0.1345			

Sorption of Alcohol from Mixtures of Alcohol and Water.

The change in the composition of the various mixtures of alcohol and water after treatment with charcoal for twenty-four hours was determined by accurately measuring the change in the density.

Mixtures of alcohol and water were carefully prepared and the density determined by the pyknometer method. Twenty-five c.c. of the mixture were measured into a well-stoppered flask of 50 c.c. capacity and two grams of purified animal charcoal, which had previously been heated in a vacuum at a dull red heat for three hours and cooled, were introduced. The flask was then placed in a thermostat at 25° and repeatedly shaken. After twenty-four hours, the charcoal was filtered off and the density of the mixture redetermined. From this new density the composition of the mixture was obtained. The results are given in Table II.

In calculating the amount of alcohol sorbed it has been assumed that no water has been sorbed during the period under observation. The error introduced is negligible, since the amount of water sorbed is so small that it would not materially affect the result. All densities were determined at 25°.

TABLE II.

Volume percentage of alcohol before sorption.	Density before sorption.	Density after sorption.	Volume percentage of alcohol after sorption.	$\frac{x}{m}$
90	0·82511	0·82678	89·59	0·504
75	0·86906	0·87100	74·26	0·3590
60	0·90581	0·90804	58·95	0·3203
50	0·92715	0·92912	48·99	0·2475
40	0·94565	0·94712	38·84	0·2368
25	0·96756	0·96864	23·74	0·2066
10	0·98482	0·98557	9·31	0·0701
5	0·99135	0·99158	4·88	0·0158

Rate of Sorption of Alcohol from Alcohol-Water Mixtures.

The rate of sorption of alcohol was determined by measuring the rate of change of density. A number of flasks were set up as before and the contents examined after different intervals of time. The results are given in Table III for 90, 50, and 5 per cent. mixtures by volume.

Discussion of Results.

The results in Table I show that the rate of sorption of water is exceedingly slow, requiring about seventy days to attain equilibrium; in the case of alcohol, equilibrium is attained in

TABLE III.

90 per cent. Mixture.

Time in hours.	Density.	Volume percentage of alcohol.	$\frac{x}{m}$
0	0.82511	90	—
24	0.82678	89.59	0.504
48	0.82711	89.49	0.554
72	0.82725	89.46	0.641

50 per cent. Mixture.

Time in hours.	Density.	Volume percentage of alcohol.	$\frac{x}{m}$
0	0.92715	50.0	—
19	0.92858	49.20	0.1988
42	0.92979	48.57	0.3475
62	0.93108	47.94	0.4918
90	0.93245	47.28	0.6452
100	0.93426	47.28	0.6452

5 per cent. Mixture.

Time in hours.	Density.*	Volume percentage of alcohol.	$\frac{x}{m}$
0	0.99154	5	—
24	0.99158	4.88	0.0158
48	0.99157	„	„
72	0.99158	„	„

* The change in density for low concentrations was so small that the results were not satisfactory, but the change in concentration was certainly very small in comparison with the results obtained at higher concentrations.

about thirty-seven days. Water is sorbed to the extent of 0.13 c.c. per gram of charcoal, whereas in the case of alcohol the value is nearly five times this amount, namely, 0.62 c.c. This result is not in agreement with that put forward by Gurvitsch, who obtained similar values for both alcohol and water with the same sorbing agent. The value for alcohol falls within the same range as that given by Gurvitsch for fuller's earth as sorbing substance, but this is probably only a coincidence.

The results given in Table II for alcohol-water mixtures show that alcohol is preferentially sorbed throughout, and, further, that the amount of alcohol sorbed in the first twenty-four hours depends on the alcohol content of the mixture. In the case of 90 per cent. alcohol the charcoal has taken up nearly five-sixths of the amount required for saturation. As the water content increases, the amount of alcohol sorbed diminishes, and where the alcohol content is less than 25 per cent. the sorption becomes very small.

From Table III it will be observed that, except for low alcohol concentration, the effect of the water is to reduce the rate of sorption of alcohol, since the charcoal finally becomes saturated with respect to alcohol. When the alcohol content had fallen to about 4.88 per cent., it was not possible to detect with certainty any further change in concentration. Langmuir explains the results of Gurvitsch as being due to a large extent to capillarity. The results here given do not support this view; the values for alcohol and water are widely different, whereas if capillarity was a fundamental phenomenon, the values should be very similar. Capillarity is a factor, without doubt, but when the sorbent is in a very finely divided state, as in the present case, it is not a fundamental factor. In any case it is a variable factor depending to a large extent on the size of the particles of the given sorbent.

Within the limits of the experiments herein described, the sorption of liquids by charcoal is not independent of the nature of the liquid. Steric hindrance, as indicated by Langmuir, varies with different liquids, and, accepting this view, it is to be expected that the volumes of different liquids sorbed by unit weight of sorbent will vary over quite a large range.

In order to test further the conclusions of Gurvitsch, experiments with other liquids have been undertaken.

THE CHEMICAL DEPARTMENT,

UNIVERSITY COLLEGE, NOTTINGHAM.

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