77. *Selective Adsorption by Activated Charcoal from Solutions containing Two Organic Acids.*

By CHARLES OCKRENT.

ALTHOUGH many investigations have been carried out on the adsorption by charcoal of single substances from solutions, there have been comparatively few attempts to investigate the simultaneous adsorption from solutions containing two or more surface-active solutes. This matter is extremely important both for the understanding of the nature of adsorption processes and for the solution of biochemical problems, since the latter are usually concerned with systems containing more than one surface-active component. Indeed, the difficulty in drawing conclusions from non-living systems for the solution of biochemical problems lies in the multiplicity of the factors involved in these systems.

It was shown by Ockrent and Butler (*J. Physical Chem.*, 1930, **34**, 2297), from an examination of the surface-tension curves of a number of aqueous mixtures of two surface-active solutes at the charged mercury interface, that if one solute was much more surface active than the other, then only the more surface-active solute appeared to be adsorbed. The few recorded investigations on direct adsorptions do not lend themselves to a critical examination of this problem of selective adsorption, since in no case do any special precautions appear to have been taken to ensure that the more surface active of the two solutes in the mixtures was present in sufficient quantity to saturate the adsorbing surface by itself. The results obtained by Rona and von Tóth (*Biochem. Z.*, 1914, **64**, 288) on the surface displacement of glucose by the urethanes, although not covering a wide range of concentration, indicate that the urethanes cause a displacement of glucose from the surface, the magnitude of which varies proportionately to their adsorption; and further, that the adsorption of glucose decreased from 42% to 2% as the homologous urethanes were used in succession to displace it. Their results are shown below :

	Conc. of glucose in the solution, mol./l.,		Conc. of urethane in the solution, mol./l.,	
Urethane.	before adsorption.	after adsorption.	before adsorption.	after adsorption.
—	0·050	0·029	—	—
Methyl	0·050	0·037	0·072	0·031
Ethyl	0·050	0·040	0·074	0·021
Propyl	0·050	0·046	0·070	0·009
*iso*Butyl	0·050	0·049	0·070	0·004

The work of Warburg and Negelein (*Biochem. Z.*, 1921, **113**, 257) and Warburg (*ibid.*, 1921, **119**, 134) on the inhibition of the oxidation of cystine and other amino-acids on charcoal by the addition of capillary-active substances is also illuminating in this connexion. Abderhalden and Foder (*Kolloid-Z.*, 1920, **27**, 49) found that, in mixtures of polypeptides or amino-acids, the solute more weakly adsorbed from pure solution is displaced in the mixture, but that the more strongly adsorbable component is even more strongly adsorbed from the mixture than from the pure solution. Recently, Kolthoff and van der Goot (*Rec. trav. chim.*, 1929, **48**, 265) have investigated the adsorption from mixtures of phenolic compounds. References to a few other papers are also given in Freundlich's "Capillary Chemistry," (2nd English Edition, 1926, p. 199).

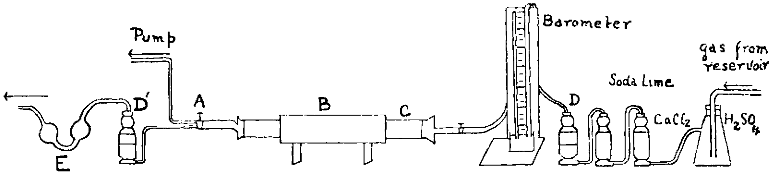
In view of these results, it appeared desirable to investigate more systematically the problem of selective adsorption by charcoal. Since most of the previous work quoted was done with blood or animal charcoals, which almost certainly contain impurities, it was decided to work with a highly purified and activated charcoal. Moreover, in order not to obscure the results, combinations of surface-active solutes were chosen which did not enter into any obvious chemical reactions, since in some cases chemical interaction might be caused at a surface although it did not occur to any appreciable extent in the homogeneous phase.

EXPERIMENTAL.

Preparation of the Charcoal.—A.R. Saccharose was heated in small portions in Royal Dresden porcelain crucibles until all fuming ceased, and then until the charcoal mass glowed strongly. The rough masses were ground in a smooth agate mortar, which had previously been subjected to high-pressure steam, and the first portions were rejected in case they contained impurities from the mortar. In this way, from about 2 kg. of sugar 350 g. of fine crystalloid charcoal were prepared.

Activation of the Charcoal.—In order to obtain results which so far as possible should be comparable, a large quantity (109 g.) of material was degassed and activated at one time, as follows. The charcoal was placed in a large, heavy-walled Pyrex tube about 30 ins. long and $1\frac{5}{8}$ ins. in diameter, fitted closely into an electric furnace which had been calibrated with a platinum–rhodium thermocouple (Fig. 1). Somewhat after the manner of Dubinin (*Z. physikal. Chem.*, 1930, *A*, **150**, 145), a Cenco Hyvac oil pump (0·001 mm.) being used, the charcoal was degassed for 3 hours at 500°, and the activation carried out at the same temperature. After degassing, the activating gas, *viz.*, atmospheric oxygen purified as in Fig. 1, was slowly admitted until the pressure in the Pyrex tube was atmospheric as shown in the barometer, the two-way stopcock *A* was then connected with the outlet tube, and the stream of activating gas passed through. The activation was continued for 2 hours at the rate of 20 litres of gas per hour and, with the 3 litres required to fill the apparatus to atmospheric pressure, a total of 43 litres was used. (Before the heating for degassing, 9 litres of activating gas were used to sweep air out of the apparatus, so the charcoal was heated in the absence of impure air.) To ensure uniform activation, the gas passed through a four-pronged Pyrex distributor which was embedded in the charcoal (Fig. 1A). From 109 g. of material, 89 g. of activated substance were obtained, and on complete ignition of 1·3210 g. in a silica crucible no detectable residue was found, so the charcoal was practically ash-free. It was stored in a tightly stoppered separating funnel with a wide-apertured stopcock and thoroughly

FIG. 1.



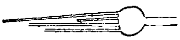


FIG. 1A.

B. *Electric furnace.*
C. *Pyrex tube.*
D and D′. *Calcium chloride and soda lime.*
E. *Pulsimeter.*

shaken, and when required, it was obtained by running it out through the opened stopcock into the adsorption tubes. The solutions were made with carbon dioxide-free, distilled water.

Adsorption Procedure.—In all the experiments, 25 c.c. of the aqueous solutions of the substances investigated were used, and placed in glass tubes with well-fitting ground-glass stoppers. The solutions were shaken with the charcoal for 1 hour by means of a slowly rotating series of discs to which the tubes were fastened by brass strips. In this way, with 4 tubes to each disc, 12 tubes could be evenly shaken at a time. The tubes were then placed in a thermostat at 25° ± 0·02° and kept for about 21 hours. The solutions were then centrifuged for 10 mins. at 7500 r.p.m. and decanted.

Analysis.—The substances investigated were weak organic acids. The solutions containing the single acids were analysed by titration with carbon dioxide-free 0·01N-sodium hydroxide solution, and a small correction was made for the absorption of carbon dioxide from the atmosphere during the titrations.

The analysis of dilute solutions of mixtures of two organic acids presents many difficulties, and after a number of trials, the following method was found to yield satisfactory results and appears capable of general application. Consider solutions containing two weak acids, HA and HB. If C_A and C_B are the concentrations of the anions, and C_H that of the hydrogen ions, the dissociation constants are defined by $C_AC_H/C_{HA} = K_1$ and $C_BC_H/C_{HB} = K_2$. Since $C_H = C_A + C_B$, we have

$$C_A^2 + C_AC_B = K_1C_{HA} \quad \text{and} \quad C_B^2 + C_AC_B = K_2C_{HB}$$

whence $$C_A = \frac{K_1C_{HA}}{\sqrt{K_1C_{HA} + K_2C_{HB}}} \quad \text{and} \quad C_B = \frac{K_2C_{HB}}{\sqrt{K_1C_{HA} + K_2C_{HB}}}.$$

Let the equivalent conductivities of the ions H, A, and B at infinite dilution be u°_H, u°_A, and u°_B, then the conductivity of the solution is approximately

$$\begin{aligned}\lambda &= C_Hu^\circ_H + C_Au^\circ_A + C_Bu^\circ_B = C_A(u^\circ_A + u_H^\circ) + C_B(u^\circ_B + u^\circ_H) \\ &= \frac{(u^\circ_A + u^\circ_H)K_1C_{HA}}{\sqrt{K_1C_{HA} + K_2C_{HB}}} + \frac{(u^\circ_B + u^\circ_H)K_2C_{HB}}{\sqrt{K_1C_{HA} + K_2C_{HB}}}\end{aligned}$$

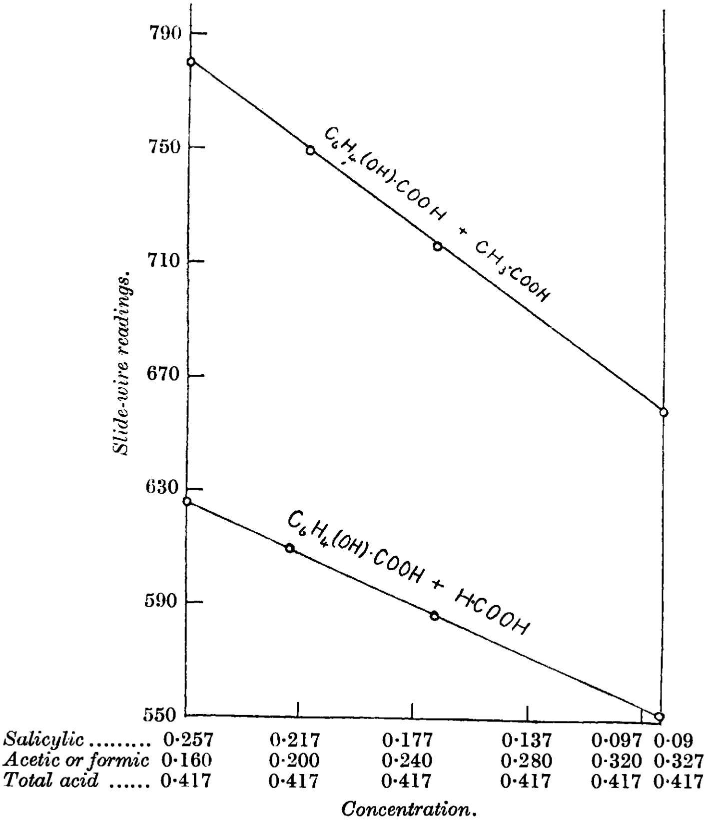
which may be written as

$$\lambda = (P_1C_{HA} + P_2C_{HB})/\sqrt{K_1C_{HA} + K_2C_{HB}}.$$

In mixtures in which the total acid concentration remains constant, so long as K_1 and K_2 are not very different, the conductivity will vary linearly with the proportions of HA and HB (Fig. 2). In practice, it is only necessary to assume that linearity holds over a much narrower range of proportions. This will be clear from the description of the procedure which is given below. After adsorption, the total acid concentration of the solution may be determined by an accurate titration with standard alkali, and hence the total acid adsorbed may be found. Now the separate amounts of the two acids adsorbed must lie between the two limits corresponding to the assumptions that HA and HB respectively are alone adsorbed. If two solutions are made, the total concentration in each being equal to the total acid concentration in the solution after adsorption, and the concentrations of the separate acids being calculated according to these assumptions, all possible values of the acid concentrations in the solution under investigation must come within these limits. If we determine the conductivity of the unknown solution and that of the two solutions corresponding to the two extreme possibilities, we may determine the proportion of the total amount absorbed which is to be ascribed to each acid.

The conductivity measurements were carried out at 25° ± 0·02°, a Kohlrausch slide wire being used with a valve oscillator as a source of current. A two-valve amplifier was employed to amplify the sound in the telephones (a loud speaker may be used instead) in the region of minimum sound, a very sharp balance point being obtained. In practice, it is not necessary to calculate the conductivity values; the direct readings of the Kohlrausch slide wire can be plotted, provided that for any given series of solutions the resistance in the balancing resistance box be kept constant. The error arising from the determination of the conductivity is negligible compared with that involved in estimating the very dilute solutions with alkali.

FIG. 2.



A blank to determine any electrolytic material (carbon dioxide, etc.) obtained from the charcoal showed that this was insignificant.

Purification of Materials.—Benzoic acid was purified by repeated sublimation, and salicylic acid (A.R.) and *o*-toluic acid by repeated recrystallisation from hot water. Acetic acid was Kahlbaum's best quality 100%, and the monochloroacetic acid was the best commercial quality obtainable. Formic acid (A.R.) and trichloroacetic acid (A.R.) were used without further purification.

Experimental Data.

Adsorption of the Acids.—Adsorption isotherms of the following acids were obtained : (*a*) Benzoic, salicylic, *o*-toluic; (*b*) monochloroacetic, acetic, formic, trichloroacetic. The adsorptions at equivalent concentrations decrease in that order.

The experimental results for the single acids are given in Table I.

TABLE I.

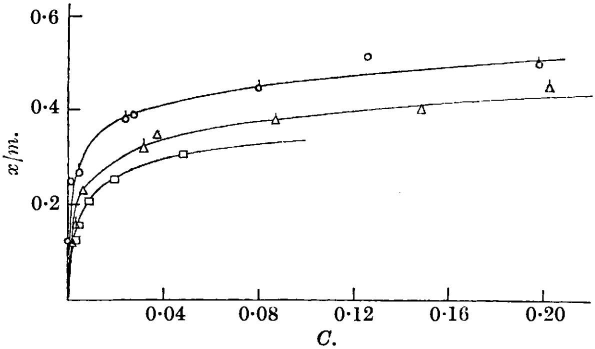
Adsorption of Separate Acids.

Initial conc. (milliequivs.).	C.	x.	x/m.
Formic acid : $m = 0{\cdot}250$ g.			
2·52	2·357	0·163	0·652
1·26	1·141	0·119	0·476
0·63	0·551	0·079	0·316
0·315	0·266	0·049	0·196
0·158	0·126	0·032	0·128
Acetic acid : $m = 0{\cdot}250$ g.			
2·49	2·243	0·247	0·988
1·245	1·081	0·164	0·656
0·623	0·508	0·115	0·458
0·312	0·243	0·069	0·276
0·156	0·116	0·040	0·160
Monochloroacetic acid: $m = 0{\cdot}250$ g.			
2·753	2·446	0·307	1·228
1·377	1·118	0·259	1·036
0·688	0·487	0·201	0·804
0·344	0·214	0·130	0·520
0·172	0·091	0·081	0·324
Trichloroacetic acid : $m = 0{\cdot}250$ g.			
1·271	1·237	0·034	0·132
0·636	0·606	0·030	0·120
0·318	0·299	0·019	0·076
0·159	0·146	0·013	0·052
Trichloroacetic acid : $m = 0{\cdot}100$ g.			
1·271	1·258	0·013	0·130
0·636	0·625	0·011	0·110
0·318	0·309	0·009	0·090
0·159	0·153	0·006	0·060
0·080	0·076	0·004	0·040

Initial conc. (milliequivs.).	C.	x.	x/m.
Benzoic acid : $m = 0{\cdot}250$ g.			
0·25	0·117	0·133	0·532
0·125	0·027	0·098	0·392
0·063	0·001	0·062	0·248
0·031	0·000	0·031	0·124
Benzoic acid : $m = 0{\cdot}100$ g.			
0·25	0·199	0·051	0·51
0·125	0·080	0·045	0·45
0·063	0·025	0·038	0·38
0·031	0·004	0·027	0·27
Salicylic acid : $m = 0{\cdot}250$ g.			
0·25	0·148	0·102	0·408
0·125	0·037	0·088	0·352
0·063	0·006	0·057	0·228
0·031	0·001	0·030	0·120
Salicylic acid : $m = 0{\cdot}100$ g.			
0·25	0·205	0·045	0·45
0·125	0·087	0·038	0·38
0·063	0·032	0·031	0·31
0·031	0·012	0·019	0·19
o-Toluic acid : $m = 0{\cdot}250$ g.			
0·125	0·048	0·077	0·308
0·084	0·020	0·064	0·256
0·063	0·009	0·054	0·216
0·042	0·003	0·039	0·156
0·031	0·000	0·031	0·124

For benzoic, salicylic, and trichloroacetic acids, isotherms were obtained with 0·250 and 0·100 g. of charcoal : the separate isotherms were in satisfactory agreement. A number of isotherms are shown in Figs. 3 and 4, the co-ordinates being x/m (x = no. of milliequivs. adsorbed, m = weight of charcoal) and C = final concentration. In all the tables and figures the concentrations refer to the number of milliequivs. per 25 c.c. of solution.

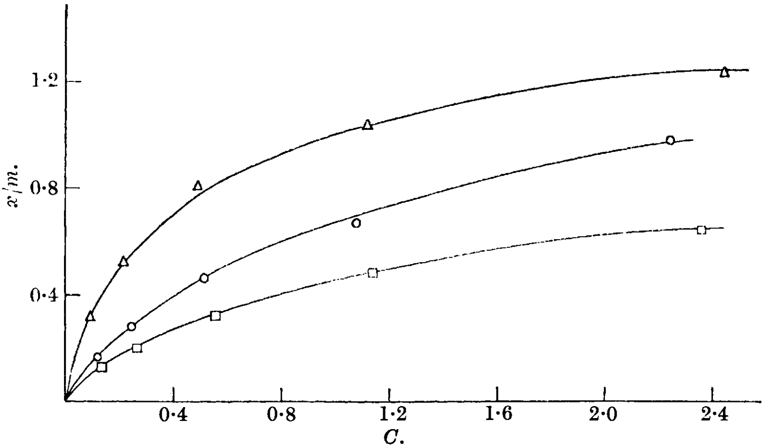
FIG. 3.



Benzoic acid -○-○- 0·250 *g. of charcoal.* -○-○- 0·100 ,, ,,
Salicylic acid -△-△- 0·250 *g. of charcoal.* △-△ 0·100 ,, ,,
o-*Toluic acid* -□-□-.

The curves for the three aromatic acids show that at the highest concentrations the adsorptions are approaching the saturation values. Those for the aliphatic acids show that the saturation values are attained much more slowly in these cases.

FIG. 4.



Acetic acid -○-○-. *Formic acid* -□-□-. *Monochloroacetic acid* -△-△-.

Adsorption of Mixtures of Acids.—The scheme was to take one of the strongly adsorbed acids at a concentration which approached the saturation adsorption value and mix this with a suitable concentration of a less strongly adsorbed acid.

The experimental data are given in Table II. In column A, which refers to the separate acid solutions, the adsorption of the less strongly adsorbed acid is expressed as a decimal of that of the

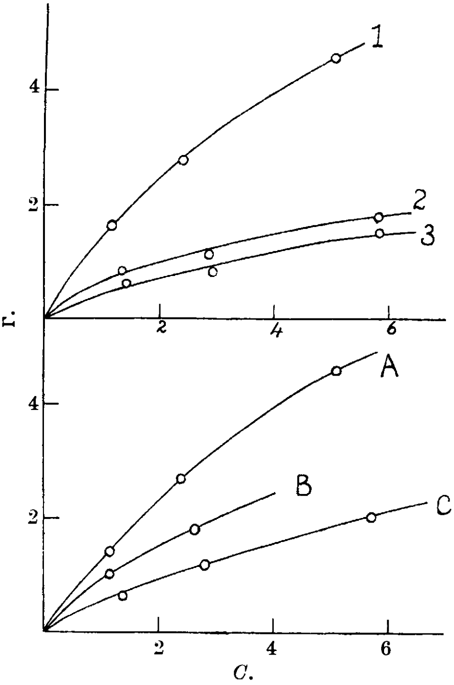
TABLE II.

Adsorption of Mixtures of Acids.

Initial conc. (milliequivs.).		Separate adsorptions.		Adsorptions from mixtures.		Adsorptions (more strongly adsorbed acid = 1).			
						A. Separate.		B. From mixtures.	
Benzoic acid (HB) and salicylic acid (HS) : m = 0·100 g.									
HB.	HS.	HB.	HS.	HB.	HS.	HB.	HS.	HB.	HS.
0·25	0·125	0·051	0·038	0·037	0·015	1	0·757	1	0·405
0·125	0·0625	0·045	0·031	0·036	0·0105	1	0·698	1	0·292
Benzoic acid (HB) and acetic acid (HAc) : m = 0·250 g.									
HB.	HAc.	HB.	HAc.	HB.	HAc.	HB.	HAc.	HB.	HAc.
0·25	0·623	0·133	0·115	0·130	0·039	1	0·859	1	0·301
0·25	0·312	0·133	0·069	0·129	0·020	1	0·520	1	0·155
0·25	0·156	0·133	0·040	0·121	0·017	1	0·303	1	0·141
0·125	0·623	0·098	0·115	0·102	0·044	1	1·167	1	0·429
0·125	0·312	0·098	0·069	0·103	0·026	1	0·706	1	0·253
0·125	0·156	0·098	0·040	0·087	0·023	1	0·411	1	0·264
Benzoic acid (HB) and formic acid (HF) : m = 0·250 g.									
HB.	HF.	HB.	HF.	HB.	HF.	HB.	HF.	HB.	HF.
0·25	0·63	0·133	0·079	0·135	0·036	1	0·594	1	0·265
0·25	0·315	0·133	0·049	0·139	0·0183	1	0·368	1	0·132
0·25	0·158	0·133	0·032	0·135	0·011	1	0·238	1	0·082
Benzoic acid (HB) and trichloroacetic acid (HX) : m = 0·250 g.									
HB.	HX.	HB.	HX.	HB.	HX.	HB.	HX.	HB.	HX.
0·25	1·271	0·133	0·034	0·099	0·0	1	0·252	1	0·0
0·25	0·636	0·133	0·030	0·121	0·0	1	0·225	1	0·0
0·125	1·271	0·098	0·034	0·098	0·0	1	0·343	1	0·0
0·125	0·636	0·098	0·030	0·103	0·0	1	0·305	1	0·0
Salicylic acid (HS) and acetic acid (HAc) : m = 0·250 g.									
HS.	HAc.	HS.	HAc.	HS.	HAc.	HS.	HAc.	HS.	HAc.
0·25	0·623	0·102	0·115	0·089	0·050	1	1·128	1	0·565
0·25	0·312	0·102	0·069	0·097	0·0313	1	0·683	1	0·323
0·25	0·156	0·102	0·040	0·101	0·016	1	0·398	1	0·158
0·125	0·312	0·088	0·069	0·079	0·045	1	0·786	1	0·570
0·125	0·156	0·088	0·040	0·086	0·0315	1	0·458	1	0·368
Salicylic acid (HS) and formic acid (HF) : m = 0·250 g.									
HS.	HF.	HS.	HF.	HS.	HF.	HS.	HF.	HS.	HF.
0·25	0·63	0·102	0·079	0·101	0·060	1	0·781	1	0·596
0·25	0·315	0·102	0·049	0·103	0·041	1	0·483	1	0·400
0·25	0·158	0·102	0·032	0·111	0·0215	1	0·312	1	0·195
o-Toluic acid (HT) and monochloroacetic acid (HY) : m = 0·250 g.									
HT.	HY.	HT.	HY.	HT.	HY.	HT.	HY.	HT.	HY.
0·125	0·688	0·077	0·202	0·0788	0·100	1	2·62	1	1·27
0·125	0·344	0·077	0·130	0·0858	0·0643	1	1·69	1	0·75
0·125	0·172	0·077	0·081	0·0826	0·027	1	1·108	1	0·327

more strongly adsorbed acid, which is taken as unity; this information is obtained from the data in Table I. In column B this is also done for the same acids at the same initial concentrations in the mixtures. In some cases in column A the more weakly adsorbed acid has values greater than unity; this is due to the fact that it is present in much larger concentration than the corresponding strongly adsorbed acid, so that, although the absolute amount adsorbed may be greater, the amount adsorbed at equivalent concentrations is less.

FIG. 5.



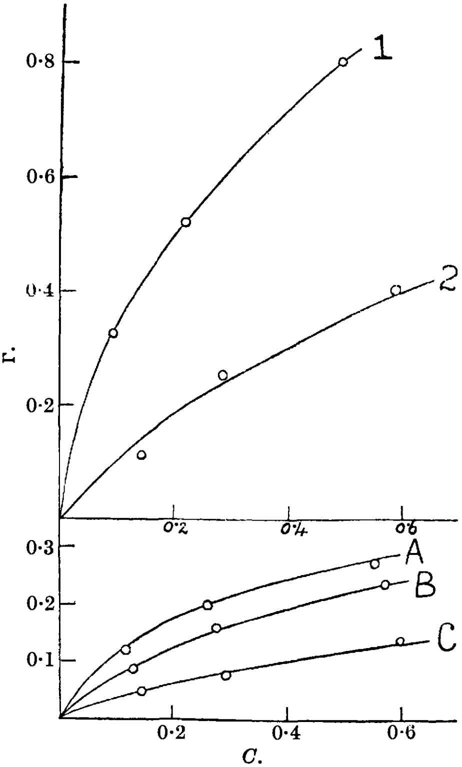
1. *Acetic acid.*
2. *Acetic acid (with* 0·25 *benzoic acid).*
3. *Acetic acid (with* 0·125 *benzoic acid).*

A. *Acetic acid.*
B. ,, ,, *(with* 0·25 *salicylic acid).*
C. ,, ,, *(with* 0·125 *salicylic acid).*

In Figs. 5 and 6 the amounts adsorbed of the weakly adsorbed acids in the single-acid solutions are compared with their amounts adsorbed in the mixtures. Although in these mixtures the amounts adsorbed of the strongly adsorbed acids, benzoic, salicylic, and *o*-toluic, vary comparatively slightly in the positive or negative direction from their amounts adsorbed when present alone, yet it is obvious that in the mixtures the adsorptions of the weakly adsorbed acids have diminished appreciably.

From Table II, cols. A and B, it is seen that in every mixture the acids are not adsorbed in amounts proportional to their adsorptions when separate, but that the normally more strongly adsorbed constituent is *selectively* adsorbed. For example, in the first case in the table, although the ratio of the separate adsorption of benzoic acid to that of salicylic acid is 1 : 0·757, yet in the mixture this becomes 1 : 0·405. With mixtures of benzoic and acetic acids this selective tendency becomes even more pronounced; this is to be expected, since acetic acid is less adsorbed than salicylic acid. Similar results are obtained with the benzoic–formic acid mixtures. In the mixtures of benzoic with trichloroacetic acid there appears to be complete selective adsorption of the former, no trichloroacetic

Fig. 6.



1. *Monochloroacetic acid.*
2. *Monochloroacetic acid* (*with* o-*toluic acid*).

A. *Formic acid.*
B. ,, ,, (*with* 0·25 *salicylic acid*).
C. ,, ,, (*with* 0·25 *benzoic acid*).

acid being adsorbed at all; the latter, being the most weakly adsorbed of all the acids investigated, as expected, shows least adsorption in the mixtures.*

In the mixtures of salicylic and acetic acids also, selective adsorption of the more strongly adsorbed salicylic acid is very marked. Moreover, since the adsorption of the latter acid is less than that of benzoic acid, it is found, as expected, that the relative decrease in the amount of acetic acid adsorbed in presence of benzoic acid is greater than in the presence of salicylic acid. Similar results are obtained with the salicylic–formic acid mixtures (Figs. 5 and 6).

In the mixtures of *o*-toluic and monochloroacetic acids strongly pronounced selective adsorption of the former acid is also found in every case.

Discussion.

Adsorption of the Acids.—According to the kinetic treatment of Langmuir (*J. Amer. Chem. Soc.*, 1918, **40**, 1360), if the rate of adsorption is proportional to the concentration of solute in the solution and to the fraction of surface unoccupied by the solute molecules, and the rate of desorption is proportional to the surface concentration (*i.e.*, the amount adsorbed), then for equilibrium,

$$k\Gamma = C(1 - A\Gamma) \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where C is the concentration of solute in the solution, A the surface area occupied by an adsorbed molecule, Γ the number of molecules adsorbed per unit area, and k a constant. Equation (1) can be written in the form

$$(1 - A\Gamma)/\Gamma = k/C \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and

$$1/\Gamma = k/C + A \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

or

$$1/\Gamma = k/C + 1/\Gamma_{\text{max.}}$$

If this equation holds, then $1/\Gamma$ plotted against $1/C$ should give a straight line, the slope of which is k, and the intercept on the axis at A, *i.e.*, where Γ is a maximum and all the available adsorbing surface is covered with a unimolecular layer of adsorbed molecules. Figs. 7 and 8 show that, except for the points representing the smallest concentrations of formic and acetic acids, the experimental data are in excellent agreement with equation (3). It thus appears that the adsorption of the acids by the activated charcoal is definitely a surface phenomenon, and is conditioned, as in the postulates of Langmuir's treatment, by a competition for the available surface

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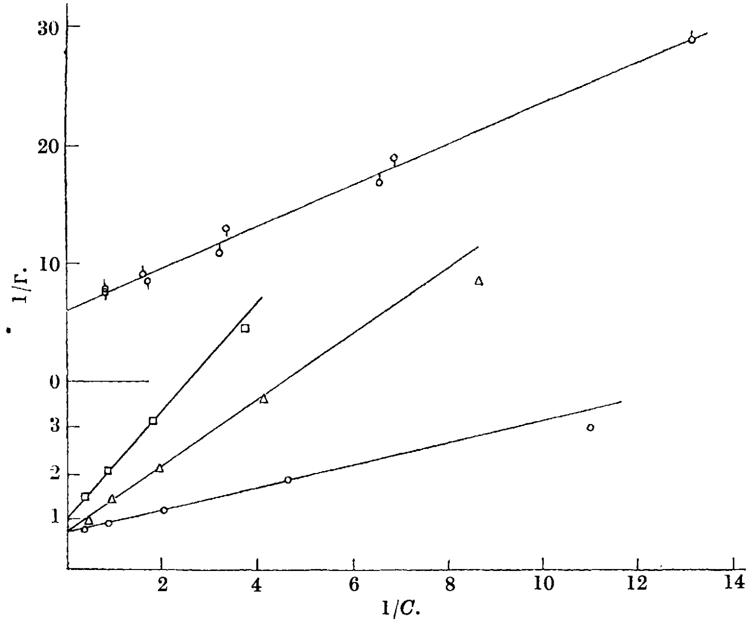
* As trichloroacetic acid is a fairly strong acid, it might invalidate the method of conductivity analysis; since, however, the conductivities of the solutions under investigation exactly coincided with those of the solutions made up on the assumption that only benzoic acid was adsorbed, this disturbing effect does not operate in these cases.

between the solute and the solvent molecules. The possibility that adsorption by charcoal is not a true surface phenomenon, but is complicated by such effects as capillary condensation, complexity

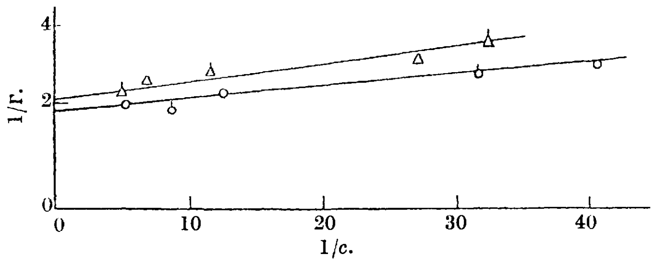
FIG. 7.



Formic acid -□-□-.
Acetic acid -△-△-.
Monochloroacetic acid -○-○-.

Trichloroacetic acid {-○-○- 0·250 *g. of charcoal.*
-ȯ-ȯ- 0·100 ,, ,,

FIG. 8.



Benzoic acid {-ȯ-ȯ- 0·250 *g. of charcoal.*
○-○ 0·100 ,, ,,

Salicylic acid {-△-△- 0·250 *g. of charcoal.*
-△̇-△̇- 0·100 ,, ,,

of the surface, etc., has been kept in mind from the outset, and the close agreement with the requirements of Langmuir's equation is regarded as satisfactory. An excellent extrapolation to the value of A(*i.e.*, $1/\Gamma_{\text{max.}}$) can be obtained from the curves; Γ, the amount adsorbed, is the experimental quantity obtained per gram of adsorbent, and as the available surface is not known, it is not possible to calculate the values of A in absolute but only in relative units. The values of A and k, and those of Γ extrapolated from the curves, for maximum adsorption are given in Table III.

TABLE III.

Acid.	$\Gamma_{\text{max.}}$ (milliequivs.).	k.	A.
$H{\cdot}CO_2H$	1·0	1·15	1·0
$CH_3{\cdot}CO_2H$	1·33	0·70	0·75
$CH_2Cl{\cdot}CO_2H$	1·33	0·25	0·75
$CCl_3{\cdot}CO_2H$	0·168	1·8	5·95
$C_6H_5{\cdot}CO_2H$	0·541	0·023	1·85
$C_6H_4(OH){\cdot}CO_2H$	0·476	0·031	2·10
$C_6H_4Me{\cdot}CO_2H$	0·37	0·019	2·7

The values of A may differ because either (1) the surface area of the charcoal available for the adsorption of the different acids is different, or (2) the available area is the same for all the acids, but that occupied by a molecule of the different acids is different. The figures are in accordance with the second hypothesis. Acetic, monochloroacetic, and formic acids have nearly the same value of A (that of formic acid being somewhat greater), whilst the value for trichloroacetic acid is about 6 times greater, and the aromatic acids have areas from 2 to 3 times that of acetic acid. The values of A obtained are in reasonable agreement with what the areas of these molecules might be expected to be.

Adsorption from Mixtures of Acids.—It has been shown by Butler and Ockrent (*J. Physical Chem.*, 1930, **34**, 2841) that Langmuir's theory can be extended to the adsorption of two solutes from solution. If the amounts of two substances adsorbed from a solution are Γ_1 and Γ_2 in which their concentrations are C_1 and C_2 and the areas occupied by the adsorbed molecules are A_1 and A_2 respectively, then the fraction of the surface area unoccupied is $1 - A_1\Gamma_1 - A_2\Gamma_2$ and for equilibrium for both solutes,

$$k_1\Gamma_1 = C_1(1 - A_1\Gamma_1 - A_2\Gamma_2) \quad . \quad . \quad . \quad . \quad (4)$$

and
$$k_2\Gamma_2 = C_2(1 - A_1\Gamma_1 - A_2\Gamma_2) \quad . \quad . \quad . \quad . \quad (5)$$

therefore
$$\Gamma_1/\Gamma_2 = k_2C_1/k_1C_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

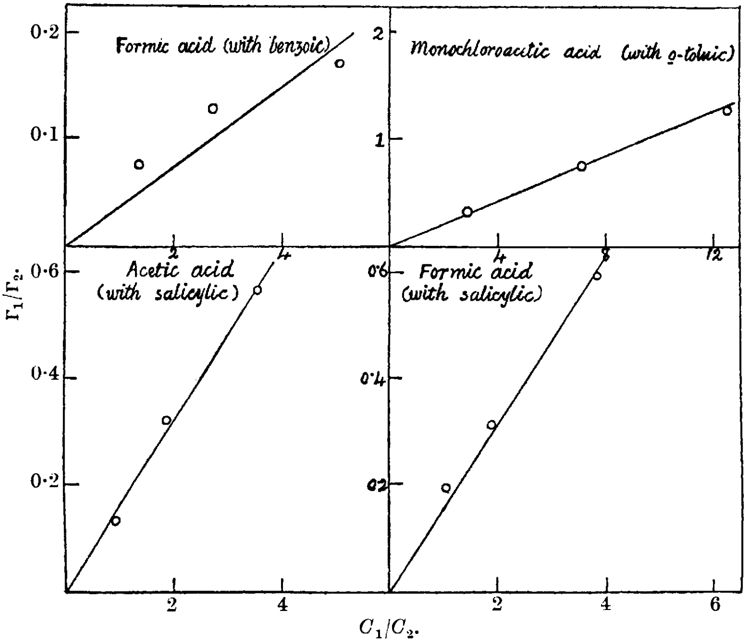
Fig. 9 shows that for most cases Γ_1/Γ_2, in accordance with (6), varies approximately linearly with C_1/C_2. The slopes of these curves should be equal to k_2/k_1; Table IV shows that in nearly all cases the observed slope is considerably greater than that calculated from the constants of the single acids.

TABLE IV.

Acid.	k_2/k_1, obs.	k_2/k_1, calc.
Formic (in 0·25 benzoic)	0·038	0·02
Acetic (in 0·25 benzoic)	0·069	0·033
Formic (in 0·25 salicylic)......................	0·160	0·027
Acetic (in 0·25 salicylic)	0·163	0·044
Monochloroacetic (in *o*-toluic)	0·10	0·076

Markham and Benton (*J. Amer. Chem. Soc.*, 1931, **53**, 497) recently applied similar equations to the adsorptions of gas mixtures by silica. They found that in mixtures of carbon monoxide and oxygen at 0° and 100°, the adsorption of each gas was diminished appreciably by the presence of the other. The oxygen adsorbed, however, was more than that calculated from the equations and the reverse was found for carbon monoxide. In mixtures of carbon dioxide with oxygen or carbon monoxide, the adsorption of the dioxide was many times greater than that of the second component, but the amounts of either carbon monoxide or oxygen adsorbed were greater than the calculated quantities. Linear curves were obtained for the mixtures of carbon monoxide and oxygen, but not for the mixtures containing carbon dioxide. The authors suggested that in some cases the anomalies might be accounted for by " a decrease

FIG. 9.



in the rate of evaporation of a given molecule by the presence in an adjacent space of a molecule of a second gas."

It is possible that similar considerations might account for the difference between the observed and calculated slopes in the cases investigated here : thus, the constant k for the adsorption of acetic acid alone by activated charcoal may differ considerably from that for the adsorption of acetic acid by a surface nearly saturated with benzoic acid. It is also possible that, when applied to molecules having different surface areas, Langmuir's equation requires modification. This equation assumes that the chance of a molecule being adsorbed is proportional to the surface area unoccupied. Now the unoccupied area will consist of patches of different sizes, some of which may be too small to receive a molecule from the solution, and its effective area will be correspondingly diminished, and the more so the greater the size of the molecule; hence the adsorption of large molecules may be expected to be less than Langmuir's equation indicates. This is, in fact, found to be the case, for we have k_2/k_1 obs. $>$ k_2/k_1 calc. or (from 6) Γ_1/Γ_2 obs. $>$ Γ_1/Γ_2 calc.; k_2 refers in all cases in Table IV to the larger (aromatic) molecule.

The mixtures of benzoic and trichloroacetic acids are of special interest, since, not only are these the most highly adsorbed and the least adsorbed substance respectively, but also the surface area occupied by the molecules of the latter is very much greater (3 times) than that occupied by the benzoic acid molecule. A competition for the vacant spaces of the adsorbing surface will be influenced by the size of the patches and will be overwhelmingly in favour of the benzoic molecules, so it is not surprising to find complete selective adsorption of the benzoic acid. The contrary is the case, however, in the mixtures of benzoic acid with the other aliphatic acids, and so, quite apart from the influence of adsorbability, the spatial effect will also be of some (though secondary) importance and to some extent will mitigate the influence of the greater adsorbability of the benzoic acid. The same considerations apply to all the other mixtures.

In the most concentrated mixtures, *i.e.*, the first member of each series in Table II, although the total amount adsorbed from the mixtures is not constant, yet the total area occupied (*i.e.*, $A_1\Gamma_1 + A_2\Gamma_2$) is very nearly the same in all cases. With the exception of mixture 3 (Table V), the total area occupied is constant within the experimental error and corresponds fairly closely to the saturation value. The figures in the last column of Table V are the calculated comparative areas. The amounts adsorbed, which are taken from Table II, are for 0·250 g. of charcoal; the adsorptions per g. are therefore 4 times these quantities, and these values are used.

TABLE V.

	Amount adsorbed, Γ_2.	Surface occupied, $A_2\Gamma_2$.	Amount adsorbed, Γ_1.	Surface occupied, $A_1\Gamma_1$.	Total surface occupied, $A_1\Gamma_1 + A_2\Gamma_2$.
1.	*Benzoic acid.*		*Acetic acid.*		
	0·520	0·962	0·156	0·117	1·08
2.	*Benzoic acid.*		*Formic acid.*		
	0·540	0·999	0·143	0·143	1·14
3.	*Salicylic acid.*		*Acetic acid.*		
	0·354	0·743	0·200	0·150	(0·89)
4.	*Salicylic acid.*		*Formic acid.*		
	0·404	0·848	0·240	0·240	1·09
5.	o-*Toluic acid.*		*Monochloroacetic acid.*		
	0·315	0·851	0·400	0·300	1·12

It has been suggested that different substances are adsorbed on different active patches of the adsorbing surface (*e.g.*, Taylor, *J. Physical Chem.*, 1926, **30**, 145). The results of this investigation support the conclusion that the adsorption of the different acids occurs on the same surface. It is, of course, possible that with substances of different types distinct adsorption areas might be found.

The agreement of the saturation adsorption areas for the mixtures seems to exclude the possibility of chemical interaction between the adsorbed acids, since the calculation of these areas involves the separate adsorption of the acids.

The phenomenon of selective adsorption, unobscured by the possibility of surface interaction between the two adsorbed solute molecules, throws considerable light on the results obtained by Phelps and Peters (*Proc. Roy. Soc.*, 1929, *A*, **124**, 584) on the adsorption of weak organic acids by charcoal. They found that the adsorption was proportional to the amount of undissociated acid, and that only the undissociated molecules appear to be adsorbed. Phelps (*ibid.*, 1931, *A*, **133**, 155) has further shown that similar considerations apply to the weak organic bases. This becomes easily explicable when it is remembered that, in accordance with the theory of selective adsorption, it is to be expected that in a mixture containing strongly adsorbable undissociated molecules and weakly adsorbable ions (arising either from the presence of salt or by slight dissociation of the acid or base), the more strongly adsorbable component will be preferentially adsorbed.

Hydrolytic Splitting.—To find how the salt of a weak organic acid behaves, measurements of the adsorption of sodium salicylate from aqueous solutions were attempted. If the sodium and salicylate ions are adsorbed in equal amounts, it is possible to determine the change of concentration of the salt by measuring the conductivities of the solution before and after adsorption, and finding the change in concentration from the concentration–conductivity curve. In all the experiments, 25 c.c. of a number of solutions were taken with 0·250 g. of charcoal, the adsorption procedure being the same as that employed with the acids. The results are in Table VI. The p_H's of the solutions were also measured before and after adsorption with the combination of a normal calomel and a bubbling hydrogen electrode.

TABLE VI.

Conc. of salt (milliequivs.).	Conductivity		p_H	
	before ads.	after ads.	before ads.	after ads.
2·5	0·0153	0·0152	6·1	7·7
1·25	0·00809	0·0079	6·1	7·8
0·625	0·00423	0·00406	6·1	7·7
0·313	0·00219	0·00202	6·9 (?)	7·8
0·157	0·00113	0·00100	7·0 (?)	7·7

The conductivity measurements do not indicate that any marked adsorption has occurred, but the p_H values have changed very markedly towards the alkaline side. If the salicylate ion alone has been adsorbed, leaving a preponderance of sodium ions in the solution, these will be neutralised by hydroxyl ions provided by hydrolytic splitting, and an equivalent amount of hydrogen ions will be available for the formation of salicylic acid in the charcoal surface; the solution will thus become alkaline and no very marked change is to be expected in the conductivity since an equivalent amount of hydroxyl ion is present in the solution to replace the salicylate taken up by the charcoal. This phenomenon of hydrolytic splitting established by Miller and his co-workers (*Colloid Symp. Monograph*, 1927, **5**, 55) is thus accounted for by the preferential adsorption of the more strongly adsorbable salicylic acid, and is fully in accord with the theory of selective adsorption.

Summary.

1. A method for determining the concentrations of mixtures of small amounts of two weak acids in solution has been devised.

2. The adsorption isotherms of benzoic, salicylic, *o*-toluic, monochloroacetic, acetic, formic, and trichloroacetic acids have been obtained at 25° ± 0·02° with activated ash-free sugar charcoal. The adsorptions at equivalent concentrations are in the order given.

3. The results obtained are in good agreement with the Langmuir adsorption isotherm, $1/\Gamma = k/C + A$ or $1/\Gamma = k/C + 1/\Gamma_{max.}$, and a finite adsorption area for the charcoal surface is indicated by the experiments.

4. The maximum adsorption ($\Gamma_{max.}$) for the different acids has

been extrapolated from the curves, and the relative areas occupied by the acid molecules have been calculated : they are in agreement with the generally accepted sizes of the molecules.

5. The adsorptions from solutions of several series of mixtures containing two acids have been determined. In no case are the amounts of the acids adsorbed proportionate to their adsorptions when separate, but in every case the strongly adsorbed acid is selectively adsorbed from the mixture. In one series of mixtures containing benzoic and trichloroacetic acids, the former is exclusively adsorbed.

6. It has been shown that, if in a series of mixtures the more strongly adsorbed acid is replaced by a rather less strongly adsorbed acid, then the depression of the adsorption of the second, weakly adsorbed, component is decreased.

7. Langmuir's theory applied to adsorptions from mixtures containing two surface active components requires that $\Gamma_1/\Gamma_2 = k_2C_1/k_1C_2$; Γ_1/Γ_2 is found to be proportional to C_1/C_2 but the proportionality constant does not agree with that calculated from the isotherms of the single acids. It is suggested that for molecules occupying different surface areas Langmuir's theory may require modification.

8. For the most concentrated mixtures of each series, while the total adsorption (in g.-mols.) of both acids from each of the different mixtures is not constant, it has been shown that the total surface area occupied by the molecules of the two adsorbed acids is constant. The results indicate that the acids are all adsorbed on the same surface of the charcoal.

9. The observations of Miller on the hydrolytic splitting of salts of weak acids by ash-free charcoal have been confirmed. The phenomenon can be accounted for as an example of selective adsorption.

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