CHAPTER VI

Effect of carbon-oxygen surface complexes on selective adsorption by carbons from binary liquid solutions
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Investigations on adsorption from solution phase proceeded, initially, by analogy with the studies which had earlier been carried out on gases. It was found that a large number of adsorption isotherms from solution phase followed the Freundlich equation (1)

\[ \frac{x}{m} = K c^{1/n} \]  \hspace{1cm} (i)

or the Langmuir equation (2)

\[ \frac{x}{m} = \frac{k_1 c}{(1 + k_1 c)} \]  \hspace{1cm} (ii)

where \( \frac{x}{m} \) is adsorption per unit mass of the adsorbent, \( c \) is the equilibrium concentration and \( k_1, n, k_1 \) are constants.

Further investigations showed that these equations were applicable only up to a certain range of concentration. Theoretically speaking, if these equations were followed over the complete concentration range, the adsorption isotherm should always show increase of adsorption with increase in concentration. Actually, however, in many cases, the curve reaches a maximum and ultimately falls to zero, or shows even a negative value of adsorption. Williams (3), while studying adsorption by charcoal from aqueous solutions, pointed out that in the case of completely miscible liquids, where the whole concentration
range is considered, the distinction between solute and solvent becomes arbitrary and that both the components may be adsorbed simultaneously. It was pointed out that it was wrong to speak of adsorption 'from' or 'in' solution (as mentioned in earlier investigations) and should be replaced by adsorption 'of' solution, thus emphasising the fact that both the solute and the solvent are likely to be adsorbed. The adsorption isotherms, obtained by plotting change in concentration against equilibrium concentration is a composite isotherm (i.e. the resultant of combining the adsorption isotherms of both the components) and not a true adsorption isotherm of that component alone whose change of concentration is being taken into consideration. This isotherm, in other words, shows as to which of the components is adsorbed to a relatively greater extent. The component which is adsorbed more is said to be 'selectively' or 'preferentially' adsorbed.

Several workers, including Williams (3), Jones and Outridge (4), Schay and Nagy (5-8), Kipling et al (9-12), and Elvin and Larenove (13), have calculated the adsorption of individual components from the composite isotherms. The relationship between the apparent adsorption and the true adsorption of each component is given by the equation (14)

\[ n_0 \Delta x/m = n_1^s (1-x) - n_2^s x \]

(iii)

where \( n_0 \) is the total number of moles of the two components
added to m g. of the adsorbent, \( \Delta x \) is the change in mole fraction of the component 1 caused by the removal of \( n_1^s \) moles of component 1 and \( n_2^s \) moles of component 2, and \( x \) is the equilibrium mole fraction of component 1. The quantity \( n_0 \Delta x/m \) when plotted against \( x \), gives the composite isotherm.

In order to calculate the values of \( n_1^s \) and \( n_2^s \) from equation (iii), Kipling and Tester (9), assuming the adsorption to be monomolecular, suggested another equation

\[
\frac{n_1^s}{(n_1^s)_m} + \frac{n_2^s}{(n_2^s)_m} = 1
\]

where \( (n_1^s)_m \) and \( (n_2^s)_m \) are the number of moles of components 1 and 2, respectively, required to form monolayers on the surface of one g. of the adsorbent. These monolayer values can be obtained by knowing the surface area of the solid and the molecular areas of the adsorbates, or alternatively, by applying the Langmuir or the B.E.T. equation to the vapour adsorption isotherm of each component. With the help of equations (iii) and (iv) it should be possible to calculate isotherms of adsorption of the individual components.

It was assumed by Kipling and Tester (9) that the adsorbed phase is one molecule thick. Schay and Nagy (5-8), also supported this view and proposed an analysis of the composite isotherms which is even more useful in certain cases.
According to them, the linear section of the isotherm indicates that the composition of the adsorbed phase remains constant along the range of concentration covered by this section. By extrapolating the linear section of the isotherm, the intercepts on the ordinates through \( x = 0 \) and \( x = 1 \) correspond to \((n_1^S)_c\) and \((n_2^S)_c\), respectively, which represent the number of moles of components 1 and 2 in the adsorbed phase in that range of concentration. Knowing these values, the thickness of the adsorbed layer, \( t \), can be calculated as,

\[
\frac{(n_1^S)_c}{(n_1^S)_m} + \frac{(n_2^S)_c}{(n_2^S)_m} = t \quad \cdots \cdots (v)
\]

Schay and Nagy applied this treatment to a number of systems and observed that, in general, adsorption from solution phase was monomolecular. According to these workers, it is possible to calculate specific surface area of an adsorbent from adsorption from binary solution data if it is assumed that the adsorbed phase is one molecule thick and if appropriate molecular areas are assigned to the two components.

In certain cases, where there is a possibility of strong interaction of chemical or quasichemical nature e.g., hydrogen bonding type of interaction between adsorbent and
one or both of the components, the adsorbed layer may be more
than one molecule thick, because there is a possibility of
formation of another layer over the chemisorbed layer (8,14).
In such cases, the value of t will be more than one and it
will not be possible to calculate the individual adsorption
values from equations (iii) and (iv). The values can,
however, be calculated by substituting the value of, t, in
equation (iv).

Several workers (3,4,8,9,12,14-21) have attempted to
explain the phenomenon of selective or preferential adsorption.
Some have concluded that the component which is taken up more
strongly individually, is also taken up selectively or
preferentially (15). The dipole moments (16) and surface
tensions (17,18) of the components also influence their
adsorbabilities, depending upon the nature of the adsorbent.

It has been pointed out by several workers (8,12,18-21)
that the nature of the adsorbent also plays an important
role in adsorption from binary solutions. Kipling et al (11,12),
for example, have pointed out that the presence of chemisorbed
oxygen on carbons imparts to it a polar character as a result
of which it exercises preferential adsorption for a more polar
component of a binary mixture. Similar observations were also
made by Hansen et al (21). However, very little is known about
the exact influence of the chemisorbed oxygen.
It appears that the effect of the chemisorbed oxygen on the selective adsorption needs further careful and systematic investigation in view of the work described in the previous chapters. It would be of interest, for example, to study the effect of different oxygen complexes on adsorption from different binary liquid mixtures containing components of different chemical nature.

The charcoal samples used in these investigations were: sugar charcoal as such, as well as after outgassing at 700 and 1000° and after treatment with hydrogen peroxide and potassium persulphate. The samples obtained by treating 1000°-outgassed charcoal with potassium permanganate and potassium persulphate were also included. All the liquids used were of high grade purity and were further purified by fractional distillation, the fraction boiling at the appropriate boiling point alone was collected. The various binary solutions examined were:

1) Methanol-benzene mixtures
2) Ethanol-benzene mixtures
3) Methanol-carbon tetrachloride mixtures
4) Ethanol-cyclohexane mixtures

The composite isotherms were obtained by plotting $n_o \Delta x/m$ against equilibrium mole fraction of the alcohol. The changes in concentration were measured interferometrically. The
FIG. 1. COMPOSITE ADSORPTION ISOTHERMS ON VARIOUS SUGAR CHARCOALS FROM METHANOL-BENZENE MIXTURES.

- Original Sugar Charcoal
- Original Sugar Charcoal Treated with H₂O₂
- Original Sugar Charcoal Treated with K₂S₂O₅
- 700°C Outgassed Sugar Charcoal
- 1000°C Outgassed Sugar Charcoal
- 1000°C Outgassed Sugar Charcoal Treated with K₂MnO₄
- 1000°C Outgassed Sugar Charcoal Treated with K₂S₂O₅

$w_m (\text{m mole/g})$

Mole fraction of Methanol
complete experimental details are given in the experimental part of the thesis.

The total combined oxygen, its disposition as acidic and non-acidic CO₂-complex as well as evolution as carbon monoxide and water vapour have already been discussed in the previous chapters and are reproduced in Table I for ready reference.

Results and Discussion

Adsorption from methanol-benzene mixtures

The composite adsorption isotherms for the various samples of charcoal are plotted in Fig.1. Most of the composite isotherms are seen to be S-shaped. Considering the isotherm on the original charcoal, it is seen that Δx, the decrease in mole fraction of methanol, increase with equilibrium mole fraction (x) of methanol till it reaches a maximum and shows a systematic fall thereafter, becoming zero when x is about 0.87 and negative beyond that. It follows, therefore, that methanol is taken up preferentially when x < 0.87 and benzene when x > 0.87. The maximum preference for methanol is observed when x ≈ 0.16 and for benzene when x ≈ 0.95. The preference for methanol extends not only to a wider range of
### Table I

Oxygen complexes and base adsorption capacities of various charcoal samples

<table>
<thead>
<tr>
<th>Description of the sample</th>
<th><em>Oxygen evolved on outgassing</em> at 1200° as (g./100 g.)</th>
<th><em>Total oxygen</em> evolved as (<em>CO</em>, CO &amp; <em>H₂O</em>) on outgassing</th>
<th><em>Base</em> capacity (<em>CO₂</em>-complex at 1200°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sugar charcoal original</td>
<td>10.7</td>
<td>8.6</td>
<td>7.7</td>
</tr>
<tr>
<td>outgassed at 700°</td>
<td>nil</td>
<td>2.5</td>
<td>0.8</td>
</tr>
<tr>
<td>&quot; 1000</td>
<td>nil</td>
<td>nil</td>
<td>nil</td>
</tr>
<tr>
<td>Original sugar charcoal treated with H₂O₂</td>
<td>13.1</td>
<td>8.8</td>
<td>7.2</td>
</tr>
<tr>
<td>&quot;  K₂S₂O₈</td>
<td>15.6</td>
<td>8.6</td>
<td>8.9</td>
</tr>
<tr>
<td>1000°-outgassed sugar charcoal treated with KMnO₄</td>
<td>2.8</td>
<td>0.4</td>
<td>1.4</td>
</tr>
<tr>
<td>&quot;  K₂S₂O₈</td>
<td>2.3</td>
<td>nil</td>
<td>1.8</td>
</tr>
</tbody>
</table>

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*Non-acidic* Total oxygen and *CO₂* evolved as *CO₂*, CO & *H₂O* adsorption.

*Base* capacity: *CO₂*-complex at 1200° adsorption.
concentration, as stated above, but is also considerably more than that of benzene. The composite isotherms for the 700°- and the 1000°-outgassed samples are also S-shaped and show similar trends, but the magnitude of the preference varies considerably. The sample outgassed at 1000°, for instance, shows a much lower maximum and the critical value of x, at which the preference is reversed, falls from 0.87 to 0.77. The sample outgassed at 700° gives the lowest value for the maximum as well as for the critical value of x which in this case lies close to 0.46. Further, in this case, the maximum preference for the alcohol is seen to be about the same as that for benzene.

The above results clearly indicate the influence of carbon-oxygen surface complexes on adsorption from methanol-benzene mixtures. The original charcoal, which contains a large amount of chemisorbed oxygen, disposed off as CO₂, CO and H₂O, shows considerable preference for methanol over most of the concentration range. The 700°-outgassed charcoal, which contains a certain amount of chemisorbed oxygen, disposed off largely as carbon monoxide, shows least preference for methanol, while the 1000°-outgassed charcoal which is essentially free of combined oxygen, shows more preference for methanol than shown by 700°-outgassed charcoal. Since, the original charcoal contains a large amount of oxygen disposed off as carbon dioxide (acidic CO₂-complex) as well as carbon monoxide and the preference for methanol decreases considerably on
outgassing the charcoal at 700° when the entire amount of the former type of oxygen gets eliminated, it is evident that it is this type of oxygen that is responsible for preferential adsorption of methanol from its solution in benzene by charcoal. The greater preference for benzene shown by the 700°-outgassed sample as compared to that shown by the 1000°-outgassed sample may be attributed to the presence of the CO-complex. As already discussed in previous chapters, a part of the oxygen in the CO-complex is present in the form of quinone groups which can undergo interaction with benzene (22). The original charcoal contain a large amount of the CO-complex as well but in spite of that it shows very strong preference for methanol. The reason is that this charcoal also contains an appreciable amount of the polar CO₂-complex which has stronger interaction with the polar methanol and overshadows the weaker interaction of quinonic groups with benzene.

In order to get further information regarding the influence of the acidic CO₂-complex, the adsorption on the samples of original charcoal treated with hydrogen peroxide and potassium persulphate, which contained much higher concentrations of this complex (cf. Table I), was examined. The composite adsorption isotherms on these samples are also included in Fig.1. It is seen that the preference for methanol
is now very much higher. In fact, methanol is seen to be preferred all along the concentration range and the S-shaped isotherms change into the U-shaped ones. Further, it is seen that the maximum preference is shown by the \( K_2S_2O_8 \)-treated sample which also contains the largest amount of the acidic \( CO_2 \)-complex.

Since the samples discussed so far, contained \( CO_2 \)-complex of the acidic type, it was thought of interest to study the adsorption on samples which contain the non-acidic \( CO_2 \)-complex. For this purpose, the samples obtained by treating 1000°-outgassed charcoal with potassium persulphate and permanganate, which contained large amounts of non-acidic complex (Table I), were taken. The composite isotherms on these samples, included in Fig. 1, are seen to be almost similar, in shape and content, to the isotherm on 1000°-outgassed charcoal before any treatment. This shows that the fixation of such a large amount of oxygen as 4.6 and 4.1 per cent on treatment with potassium permanganate and persulphate, respectively, makes hardly any change in the preference of the charcoal. The view of the previous workers \( (12,14,21) \) that the combined oxygen as such introduces polarity at the surface and alters preference for polar components of binary mixtures needs revision in the light of the observations recorded above.
FIG. 2. COMPOSITE ADSORPTION IsoTHEMS ON VARIOUS SUGAR CHARCOALS FROM ETHANOL-BENZENE MIXTURES.

- O - O  ORIGINAL SUGAR CHARCOAL
- △ - △  ORIGINAL SUGAR CHARCOAL TREATED WITH H₂O₂
- □ - □  ORIGINAL SUGAR CHARCOAL TREATED WITH K₂S₂O₈
- ▢ - ▢  700°C-OUTGASSED SUGAR CHARCOAL
- X - X  1000°C-OUTGASSED SUGAR CHARCOAL
- ■ - ■  1000°C-OUTGASSED SUGAR CHARCOAL TREATED WITH KMnO₄
- ● - ●  1000°C-OUTGASSED SUGAR CHARCOAL TREATED WITH K₂S₂O₈

\[ \text{nox/m. (m. mole/g)} \]

Mole fraction of Ethanol
Only a part of the combined oxygen (present as the acidic CO₂-complex), introduces polarity, another part of the chemisorbed oxygen (present as the non-acidic CO₂-complex) had hardly any effect, while still another part (evolved mostly as carbon monoxide) on the contrary, renders the surface benzophillic.

**Ethanol-benzene mixtures**

The composite isotherms of ethanol-benzene mixtures on the various samples of charcoal are plotted in Fig.2. The original charcoal, again, shows a considerable preference for ethanol over most of the concentration range. The 1000°-outgassed sample shows this preference to a much smaller extent while the 700°-outgassed sample shows this to the least extent. In fact, the last mentioned sample shows greater preference for benzene over a greater part of the concentration range. These results are similar to those obtained in the case of methanol-benzene mixtures.

The composite isotherms on the samples obtained after treatment of the original charcoal with hydrogen peroxide and potassium persulphate are U-shaped and show much greater preference for ethanol than that shown by the original charcoal throughout the entire concentration range. The K₂S₂O₈-treated sample, which contained the largest amount of the acidic CO₂-complex, also shows the highest preference for ethanol. The
formation of the non-acidic CO$_2$-complex on 1000°C-outgassed charcoal, as a result of treatment with aqueous potassium persulphate and permanganate, does not produce any significant change in the preference of the charcoal as is clear from Fig. 2.

On comparing the isotherms of methanol-benzene mixtures (Fig. 1) with those of ethanol-benzene mixtures (Fig. 2), it is seen that, for a given sample of charcoal, methanol is taken up to a greater extent than ethanol from their respective mixtures with benzene for the same value of x. This appears to be due to the smaller molecular area of methanol, so that a larger number of methanol molecules than those of ethanol, are required to complete the same thickness of the adsorbed layer. It has also been shown earlier that methanol can be more firmly held or even chemisorbed by carbons coated with the CO$_2$-complex (23). According to Kipling and Gasser (12) also, methanol, on account of greater proportion of the polar group in the molecule, can be adsorbed more readily at sites containing oxygen groups.

Carbon blacks, which are free of oxygen, generally show preference for benzene to methanol (12). However, the 1000°C-outgassed charcoal, which is also free of oxygen, shows slightly greater preference for methanol or ethanol than for benzene. The reason for this appears to be that, unlike carbon blacks, charcoals are porous materials and, therefore, some of the
FIG. 3. COMPOSITE ADSORPTION ISOTHERMS ON VARIOUS SUGAR CHARCOALS FROM METHANOL-CARBON TETRACHLORIDE MIXTURES.

- Original Sugar Charcoal
- 700° Outgassed Sugar Charcoal
- 1000° Outgassed Sugar Charcoal
- Original Sugar Charcoal Treated with H₂O₂
- Original Sugar Charcoal Treated with K₂S₂O₈
- 1000° Outgassed Sugar Charcoal Treated with K₂S₂O₄
- 1000° Outgassed Sugar Charcoal Treated with KMnO₄
finer capillary pores may not be so easily accessible to benzene as to methanol or ethanol.

**Methanol-carbon tetrachloride mixtures**

The composite isotherms for adsorption of methanol-carbon tetrachloride mixtures on various charcoals are given in Fig. 3. It is seen that, in this case, \( \Delta x \) always remains positive at all values of \( x \). This shows that methanol is being preferred throughout the entire concentration range by all the charcoal samples, used, although the magnitude of the preference varies considerably from charcoal to charcoal, generally decreasing with decrease in oxygen content. The preference for carbon tetrachloride is not noted in any case and the isotherms are all U-shaped. It is interesting to note that the 700\(^\circ\)-outgassed charcoal does not show any departure from this general behaviour. This confirms, that its anomalous behaviour in the case of methanol-benzene and ethanol-benzene mixtures is due to the interaction of benzene with quinone structures present on the surface.

The preference for methanol is seen to increase on extending the amount of the acidic CO\(_2\)-complex by treating the original charcoal with hydrogen peroxide or potassium persulphate. However, the fixation of oxygen as non-acidic CO\(_2\)-complex, as on treating 1000\(^\circ\)-outgassed charcoal with
FIG. 4. COMPOSITE ADSORPTION ISOTHERMS ON VARIOUS SUGAR CHARCOALS FROM ETHANOL-CYCLOHEXANE MIXTURES.

- O-----O- ORIGINAL SUGAR CHARCOAL
- △△△ 700° OUTGASSERTED SUGAR CHARCOAL
- x--x--x 1000° OUTGASSERTED SUGAR CHARCOAL
- ●●● ORIGINAL SUGAR CHARCOAL TREATED WITH H₂O₂
- ▲▲▲ ORIGINAL SUGAR CHARCOAL TREATED WITH K₂S₂O₈
- □□□ 1000° OUTGASSERTED SUGAR CHARCOAL TREATED WITH KMnO₄

MOLAR ABSORPTION COEFFICIENT (mol. moles/g)

MOLE FRACTION OF ETHANOL
potassium persulphate or potassium permanganate, does not seem to introduce much change (Fig. 3). These results, again, support the view that the non-acidic complex has little or no effect in altering surface behaviour of charcoals.

On comparing the composite isotherms of methanol-benzene mixtures (Fig. 1) and methanol-carbon tetrachloride mixtures (Fig. 3), it is seen that methanol is adsorbed more from its mixtures with carbon tetrachloride than from its mixtures with benzene by all the charcoal samples used. This is due to greater interaction of benzene than that of carbon tetrachloride with charcoal surface on account of the presence of quinone structures, as already discussed.

**Ethanol-cyclohexane mixtures**

The composite isotherms for ethanol-cyclohexane mixtures on various charcoal samples are plotted in Fig. 4. These isotherms are also U-shaped indicating preference for ethanol at all concentrations.

The original charcoal shows considerable preference for ethanol. This preference increases on treating the charcoal with potassium persulphate and hydrogen peroxide, when the CO₂-complex is extended, and decreases on evacuating the charcoal at 700°C when the CO₂-complex is eliminated. There
is no significant change in preference when the charcoal is outgassed between 700 and 1000° or when 1000°-outgassed charcoal is treated with any of the oxidising solutions, showing that the oxygen present as CO-complex or that present as non-acidic CO₂-complex makes no significant alteration in surface interactions.

The thickness of the adsorbed layer

The amounts of the various adsorbates required to form complete monolayers on one gram of the adsorbent are given in Table II. Since, as already mentioned in the previous chapter, the surface area of the charcoal does not undergo any significant change either on evacuating at temperatures up to 1000° or on treatment with the various oxidising solutions, the surface area of all the samples of sugar charcoal was taken as 420 m²/g. While calculating the monolayer values, the molecular areas of the various liquids were taken as reported by Kipling et al (24), which have also been included in Table II.

It is seen from the composite isotherms (Figs. 1-4) that almost all the curves show a linear or nearly linear section, indicating that the composition of the adsorbed phase in the concentration range represented by the linear section remains about the same. In such cases, it is possible to determine the composition of the adsorbed phase in the linear section
Table II

Molecular areas and the amounts of various adsorbates required to form a monolayer on charcoal.

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>Molecular area ($\text{Å}^2$)</th>
<th>Monolayer value (Millimoles/g.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>16.7</td>
<td>4.38</td>
</tr>
<tr>
<td>Ethanol</td>
<td>25.4</td>
<td>2.75</td>
</tr>
<tr>
<td>Benzene</td>
<td>44.0</td>
<td>1.61</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>37.0</td>
<td>1.89</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>48.0</td>
<td>1.45</td>
</tr>
</tbody>
</table>

* Surface area of charcoal samples taken as 420 m$^2$/g.
of the curve by extrapolating the linear section to $x = 0$ and $x = 1$, as already discussed. Knowing these values (which represent $(n_1^S)_c$ and $(n_2^S)_c$ of equation IV), it is possible to calculate the thickness of the adsorbed layer.

The values for the thickness of the adsorbed layer, due to each component as well as the total, are given in Tables III and IV. It is seen that the molecular thickness is greater than unity in those cases in which the charcoal samples contain the acidic CO$_2$-complex. For instance, in the case of adsorption from methanol-benzene mixtures, the molecular thickness on the original charcoal, as well as on the samples obtained after its treatment with H$_2$O$_2$ and K$_2$S$_2$O$_8$, is even $> 2$ - the K$_2$S$_2$O$_8$-treated sample showing the highest value. The outgassed samples show much less thickness which, however, is, again, more than unity. The contribution of methanol towards the thickness of the adsorbed layer is also seen to increase with increase in the amount of the acidic CO$_2$-complex. The other systems also show similar trends.

The multimolecular adsorption observed in these investigations can be attributed to the heterogeneity of charcoal surface. In the case of the original charcoals, the presence of the acidic CO$_2$-complex provides polar sites where
### Table III

Thickness of the adsorbed layer in the case of adsorption from methanol-benzene and ethanol-benzene mixtures on various sugar charcoals

<table>
<thead>
<tr>
<th>Description of the sample</th>
<th><em>Methanol-benzene system</em></th>
<th><em>Ethanol-benzene system</em></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Methanol</td>
<td>Benzene</td>
</tr>
<tr>
<td>Sugar charcoal original</td>
<td>1.39</td>
<td>1.11</td>
</tr>
<tr>
<td>&quot; outgassed at 700°</td>
<td>0.36</td>
<td>0.94</td>
</tr>
<tr>
<td>&quot; 1000°</td>
<td>0.84</td>
<td>0.49</td>
</tr>
<tr>
<td>Original sugar charcoal treated with $H_2O_2$</td>
<td>1.70</td>
<td>0.70</td>
</tr>
<tr>
<td>&quot;  $K_2S_2O_8$</td>
<td>1.93</td>
<td>0.62</td>
</tr>
<tr>
<td>1000°-outgassed sugar charcoal treated with $K_2S_2O_8$</td>
<td>0.77</td>
<td>0.73</td>
</tr>
<tr>
<td>&quot;  $KMnO_4$</td>
<td>0.75</td>
<td>0.75</td>
</tr>
</tbody>
</table>
Table IV

Thickness of the adsorbed layer in the case of adsorption from methanol-carbon tetrachloride and ethanol-cyclohexane mixtures on various charcoals

<table>
<thead>
<tr>
<th>Description of the sample</th>
<th>Molecular thickness of the adsorbed layer in the case of:</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Methanol-carbon tetrachloride system</td>
<td>Ethanol-cyclohexane system</td>
</tr>
<tr>
<td></td>
<td>Methanol</td>
<td>Carbon tetrachloride</td>
</tr>
<tr>
<td>Sugar charcoal original</td>
<td>1.74</td>
<td>0.42</td>
</tr>
<tr>
<td>&quot; outgassed at 700°</td>
<td>1.16</td>
<td>0.40</td>
</tr>
<tr>
<td>&quot; outgassed at 1000°</td>
<td>1.01</td>
<td>0.28</td>
</tr>
<tr>
<td>Original sugar charcoal treated with H₂O₂</td>
<td>2.60</td>
<td>0.28</td>
</tr>
<tr>
<td>&quot; &quot; K₂S₂O₈</td>
<td>3.03</td>
<td>0.22</td>
</tr>
<tr>
<td>1000°-outgassed sugar charcoal treated with K₂S₂O₈</td>
<td>1.09</td>
<td>0.45</td>
</tr>
<tr>
<td>&quot; &quot; KMnO₄</td>
<td>1.04</td>
<td>0.44</td>
</tr>
</tbody>
</table>
FIG. 6: INDIVIDUAL ADSORPTION ISOTHERMS OF METHANOL AND BENZENE FROM THEIR MIXTURES ON VARIOUS SUGAR CHARCOAL SAMPLES.

(a) 1000° OUTGASSED SUGAR CHARCOAL
- MOLE FRACTION OF METHANOL
- MOLE FRACTION OF BENZENE

(b) 1000° OUTGASSED SUGAR CHARCOAL (K₂S₂O₈ TREATED)
- MOLE FRACTION OF METHANOL
- MOLE FRACTION OF BENZENE

(c) 1000° OUTGASSED SUGAR CHARCOAL (KMnO₄ TREATED)
- MOLE FRACTION OF METHANOL
- MOLE FRACTION OF BENZENE
FIG. 5. INDIVIDUAL ADSORPTION ISOTHERMS OF METHANOL AND BENZENE FROM THEIR MIXTURES ON VARIOUS SUGAR CHARCOAL SAMPLES.

(a) ORIGINAL SUGAR CHARCOAL

(b) ORIGINAL SUGAR CHARCOAL (H₂O₂-TREATED)

(c) ORIGINAL SUGAR CHARCOAL (K₂S₂O₈-TREATED)

(d) 700°C OUTGASSED SUGAR CHARCOAL

- MOLE FRACTION OF METHANOL
- MOLE FRACTION OF METHANOL
- AMOUNT ADSORBED (millimoles/g)
methanol and ethanol, of the binary mixtures, can be held strongly through hydrogen bonding, thus presenting an 'alkylated' surface on which further adsorption can take place. This has been observed by other workers as well (8,14). Similarly, 700°-outgassed charcoals, due to the presence of quinonic groups, can provide active sites where benzene can be held strongly and further adsorption can take place on this layer.

The thickness of the adsorbed layer on the 1000°-outgassed charcoal, which is essentially free of oxygen, is seen to be only a little higher than unity.

**Individual adsorption isotherms**

The individual adsorption isotherms in the case of the various systems were calculated from the respective composite isotherms with the help of equations (iii) and (iv) putting $t$, the value of thickness of the adsorbed layer, instead of $l$, in equation (iv).

The individual adsorption isotherms calculated for the methanol-benzene system have been plotted in Figs 5 and 6. These isotherms bring out clearly the influence of the oxygen complexes on adsorption from binary mixtures. The original charcoal, for example, takes more of methanol than of benzene at all concentrations except when the concentration of methanol
FIG. 6: INDIVIDUAL ADSORPTION ISO-THERMS OF ETHANOL AND BENZENE FROM THEIR MIXTURES ON VARIOUS SUGAR CHARCOAL SAMPLES.
FIG. 7. INDIVIDUAL ADSORPTION ISOTHERMS OF ETHANOL AND BENZENE FROM THEIR MIXTURES ON VARIOUS SUGAR CHARCOAL SAMPLES.

(a) ORIGINAL SUGAR CHARCOAL

(b) ORIGINAL SUGAR CHARCOAL (H₂O₂-TREATED)

(c) ORIGINAL SUGAR CHARCOAL (K₂S₂O₈-TREATED)

(d) 700°C OUTFAGSED SUGAR CHARCOAL
is too low and that of benzene too high in the mixture (Fig. 5a). Adsorption of methanol is seen to increase when the acidic CO$_2$-complex is extended on treatment with hydrogen peroxide or potassium persulphate (Fig. 5b and (c)). The 700$^\circ$-outgassed sample shows the lowest preference for methanol. The 1000$^\circ$-outgassed sample shows somewhat greater preference for methanol than that shown by 700$^\circ$-outgassed sample, which however, remains almost unaffected on building up the non-acidic CO$_2$-complex on treatment with potassium persulphate or potassium permanganate (Fig. 6(a),(b) and (c)).

The individual isotherms of adsorption, calculated for the ethanol-benzene mixture, on various samples are given in Figs. 7 and 8. It is seen that the original charcoal adsorbs more ethanol than benzene. The adsorption of ethanol increases on treatment with H$_2$O$_2$ or K$_2$S$_2$O$_8$ but decreases on outgassing the charcoal. The 1000$^\circ$-outgassed sample shows much less adsorption of ethanol while the 700$^\circ$-outgassed sample shows the least adsorption of ethanol. In the last case, the adsorption of benzene is seen to be more than that of ethanol. The samples obtained after treatment of the 1000$^\circ$-outgassed charcoal with K$_2$S$_2$O$_8$ or KMnO$_4$ show only slight increase in the adsorption of ethanol. These results also point towards the conclusions already arrived at from a study of the composite isotherms.

The individual adsorption isotherms, calculated from the composite isotherm for the methanol-carbon tetrachloride system.
FIG. 12. INDIVIDUAL ADSORPTION ISOTHERMS OF ETHANOL AND CYCLOHEXANE FROM THEIR MIXTURES ON VARIOUS SUGAR CHARCOAL SAMPLES.

(a) 1000° OUTGASSED SUGAR CHARCOAL (X2S2O5-TREATED)

(b) MOLE FRACTION OF ETHANOL

(c) MOLE FRACTION OF ETHANOL

AMOUNT ADSORBED (milli moles/g)

AMOUNT ADSORBED (milli moles/g)
FIG. II. INDIVIDUAL ADSORPTION ISOTHERMS OF ETHANOL AND CYCLOHEXANE FROM THEIR MIXTURES ON VARIOUS SUGAR CHARCOAL SAMPLES.

(a) ORIGINAL SUGAR CHARCOAL

(b) ORIGINAL SUGAR CHARCOAL (H₂O₂-TREATED)

(c) ORIGINAL SUGAR CHARCOAL (K₂S₂O₈-TREATED)

(d) 700°C-OUTGASED SUGAR CHARCOAL

MOLE FRACTION OF ETHANOL

AMOUNT ADSORBED (mili moles/g)

-0.0 0.2 0.4 0.6 0.8

-0.0 0.2 0.4 0.6 0.8

-0.0 0.2 0.4 0.6 0.8

-0.0 0.2 0.4 0.6 0.8

ETHANOL

CYCLOHEXANE

ETHANOL

CYCLOHEXANE

ETHANOL

CYCLOHEXANE
FIG. 10. INDIVIDUAL ADSORPTION Isotherms of Methanol and Carbon Tetrachloride from their Mixtures on Various Sugar Charcoal Samples.
FIG. 9: INDIVIDUAL ADSORPTION ISOTHERMS OF METHANOL AND CARBON TETRACHLORIDE FROM THEIR MIXTURES ON VARIOUS SUGAR CHARCOAL SAMPLES.

ORIGINAL SUGAR CHARCOAL ($H_2$O$_2$-TREATED)

CARBON TETRACHLORIDE

METHANOL

MOLE FRACTION OF METHANOL

AMOUNT ABSORBED (Milli moles/90)

OUTGASSED SUGAR CHARCOAL

METHANOL

CARBON TETRACHLORIDE

MOLE FRACTION OF METHANOL
(Figs. 9 and 10) as well as for the ethanol-cyclohexane system (Figs 11 and 12) also support the above observations. It is seen that the polar component is adsorbed to a greater extent than the non-polar one on all the adsorbents. But when the acidic CO₂-complex is present, the adsorption of the polar component increases further in proportion to the amount of such complex. The CO-complex and the non-acidic CO₂-complex do not seem to effect the adsorption of the polar component.

Thus, the present investigations reveal clearly the influence that the various surface carbon-oxygen complexes exercise on adsorption from binary liquid mixtures.
REFERENCES


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