PREDICTION OF BINARY ADSORPTION EQUILIBRIA OF SOLVENT AND WATER VAPOR ON ACTIVATED CARBON

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A new method is proposed to predict adsorption equilibria of mixtures of solvent and water vapor on activated carbon. It is based on evaluating the amounts of solvent and water in the capillary condensed phase in the fine pores and in the ordinary adsorbed phase in the coarse pores, respectively. Predicted results are compared with experimental ones on two kinds of activated carbons having different pore-size distributions for water-soluble solvents (methanol and acetone) and water-insoluble solvents (benzene and toluene), respectively. Both results agree fairly well.

Introduction

Recently the adsorption process of removing and recovering organic solvents from air by activated carbon has been attracting special interest from the aspect of protecting the environment from pollution. In most cases, water vapor coexists in the range from low concentration to nearly saturated state, and the concentration of solvent vapor is low. Thus it is important to evaluate the influence of humidity on adsorption equilibria of organic solvents. When humidity is high, capillary condensation of water vapor takes place and the adsorption of solvents is hindered\(^1\).

A number of methods\(^1,8,5,11\) has been proposed to predict an adsorption equilibrium of mixtures from the isotherms of the single components. However, they cannot be applied to the case with capillary condensation to be studied here.

The purpose of the present paper is to predict the adsorption equilibria for mixtures of solvent vapor in the range of low concentration and water vapor which causes capillary condensation in fine pores of the carbons. Predicted values are compared with experimental ones.

1. Method for Prediction

1.1 Model of adsorption with capillary condensation

In the case with capillary condensation, it seems better to evaluate the amount adsorbed of each component as the sum of the amount due to capillary condensation in the fine pores and the vapor-phase adsorption onto the "dry surface", which means the surface of pores where capillary condensation does not take place.

For the dry surface, the following assumption is provided to estimate the amount adsorbed.

**Assumption 1**: On the dry surface there usually exists only vapor-phase adsorption of organic solvent, and the amount adsorbed of water vapor is negligibly small because hydrophilic sites are far fewer than hydrophobic ones.

In the condensed phase, on the other hand, there take place the dissolution of organic component from the gas phase and successive liquid-phase adsorption onto the "wet surface", which means the surface of the pores where capillary condensation occurs. **Figure 1** illustrates the adsorption model mentioned above.

According to the above model, the amount of water vapor adsorbed \(q_w\) is given as that in the condensed phase. The amount of organic solvent is expressed as the sum of that adsorbed on the dry surface \(q_{o1}\), that dissolved into the condensed phase \(q_{o2}\) and that adsorbed onto the wet surface by liquid-phase adsorption \(q_{o3}\).

\[
q_o = q_{o1} + q_{o2} + q_{o3}
\]

Provided that liquid-phase adsorption occurs uni-
formly on the surface of activated carbon independent-
ly of pore radius, the amount of solvent adsorbed onto
the wet surface $q_{oZ}$ is given as Eq. (2).

$$q_{oZ} = q_{oZ}^{S} S_{o}/S_{T}$$  \hspace{1cm} (2)

where $q_{oZ}^{S}$ denotes the equilibrium amount of liquid-
phase adsorption at the composition of capillary
condensed phase, which can be determined by a
separate liquid-phase adsorption experiment.

The volume of free liquid of condensed phase is
given by subtracting the volume of adsorbate on the
wet surface from $V_c$, and the amount of solvent dissolv-
ed $q_{o2}$ is expressed by Eq. (3).

$$q_{o2} = \rho_{w} (V_c - q_{oZ}/\rho_{w})$$  \hspace{1cm} (3)

Similarly to the above, the amount of water in the
condensed phase is given by Eq. (4).

$$q_w = \rho_w (V_c - (q_{oZ} + q_{o2})/\rho_{w})$$  \hspace{1cm} (4)

The amount adsorbed of solvent on the dry surface is
given as Eq. (5) according to Assumption 1.

$$q_{oZ} = q_{oZ}^{S} S_{o}/S_{T}$$  \hspace{1cm} (5)

where $q_{oZ}^{S}$ is the equilibrium amount adsorbed of the
solvent in the pure component system.

1.2 Volume and surface area of capillary condensed phase

It has been reported that the cumulative pore volume curve calculated from the desorption isotherm of
water vapor is approximately equal to that from the
isotherm of nitrogen on activated carbon, if a suitable
contact angle $\alpha$ (cos $\alpha \approx 0.6$) for water is chosen$^{6,10}$. Hence the cumulative pore volume curve is considered to be calculated from the desorption isotherm of water vapor (as shown in Fig. 2) by using the Kelvin equation, if pores are cylindrical.

$$r = -2\sigma V_L \cos \alpha / (RT \ln p/p_s)$$  \hspace{1cm} (6)

That is to say, in choosing $r/\cos \alpha$ instead of $p/p_s$ as abscissa, the cumulative pore volume curve can be obtained as shown in Fig. 3. The cumulative surface area is expressed as

$$S = 2 \cos \alpha \sum_{r} r AV/\pi$$  \hspace{1cm} (7)

where $\Delta V$ is the increase of pore volume between
$r/\cos \alpha$ and $(r + \Delta r)/\cos \alpha$, and $r$ means the average pore radius between $r$ and $(r + \Delta r)$. The cumulative surface area curves calculated by Eq. (7) are also shown in Fig. 3.

The Kelvin equation for a multicomponent system is given as Eq. (8) by assuming that the effect of curvature on the composition of capillary condensed phase is negligible under the conditions of the present work$^{2}$ (see Appendix).

$$r = -2\sigma V_L \cos \alpha / (RT \ln p_T/p_f)$$  \hspace{1cm} (8)

where $p_T$, $\alpha$ and $V_L$ change with the composition of the
condensed phase which is determined from the iso-
thermal vapor-liquid equilibrium. Accordingly the
volume and surface area of capillary condensed phase
can be determined by Eq. (8) and Fig. 3.

Figure 2 shows the adsorption hysteresis of water vapor for two kinds of activated carbons. The
hysteresis is assumed to be mainly due to the difference
between contact angle $\alpha$ in the adsorption step and
that in the desorption step. Namely, $r$ evaluated by
Eq. (6) in the adsorption is smaller than in the desorp-
tion. When solvent vapor is adsorbed, the solvent
molecules adsorbed appreciably modify the contact
angle $\alpha$. Thus in the present work two extreme cases are discussed.

1) Case 1. Water-soluble solvent The following assumption to calculate the volume of capillary condensed phase is adopted.

Assumption 2: By the adsorption of water-soluble sol-
vant, the surface of activated carbon becomes ap-
parently hydrophilic even in the adsorption step, giving the same contact angle $\alpha$ as that in the desorp-
tion step of water.

According to Assumption 2, it is assumed that the
isotherm of the mixture of water-soluble solvent and
water vapor shows no hysteresis. Then $V_c$ and $S_c$
can be calculated from Eq. (8) and Fig. 3.

2) Case 2. Water-insoluble solvent In this case, Eq. (8) is reduced to Eq. (6). Then the next assump-
tion to calculate the volume of capillary condensed phase is introduced.

Assumption 3: In the case of water-insoluble solvent, the contact angle \( \alpha \) is the same as that for the single component isotherm of water vapor in both adsorption and desorption steps.

According to Assumption 3, the isotherm of the mixture has a hysteresis similar to that for water vapor, and \( V_c \) can be evaluated from the isotherm of water vapor (Fig. 2) and Eq. (6). \( S_o \) in the adsorption step is evaluated from Fig. 3, for \( V_c \) equal to the amount adsorbed of water in the pure component system of the same pressure (Fig. 2).

According to the present method, \( q_s \) and \( q_w \) can be calculated independently of \( \alpha \) by using Eqs. (2), (3), (4) and (5).

2. Experimentals

Adsorption equilibria for the mixtures of solvent and water were determined in both adsorption and desorption steps to verify the model proposed in this study. Acetone and methanol of research grade (water-soluble solvents) and benzene and toluene of research grade (water-insoluble solvents) were used. Two kinds of activated carbons having different adsorption properties for water vapor and different pore size distributions were used. The properties of these carbons are listed in Table 1.

1) Determination of equilibria in adsorption step

Figure 4 shows the flow-type experimental apparatus used. After air (or nitrogen) from a gas cylinder at a certain constant flow rate was dehumidified in a dryer, part of it was diverted to a water saturator and returned to the main dry air stream to permit adjustment of the humidity to a certain level. A part of the mixed stream was then diverted to a solvent saturator and returned to the main stream to obtain an arbitrary concentration of solvent vapor. This final stream was introduced to an adsorption cell of activated carbon.

The adsorption cell and saturator were immersed in temperature-controlled water baths at 30°C. The whole apparatus was placed in a temperature-controlled chamber at 34°C to prevent condensation of water vapor in the line to the adsorption cell even at high concentration.

The concentration of solvent and water vapor was analysed by a thermal conductivity detector and a flame ionization detector of the gas chromatograph.

The adsorption isotherms of the pure component systems were determined from the increase in weight of the adsorption cell.

The equilibria of mixed vapor systems were determined as follows. First, the weight increase of the cell \( W_r \) was measured after equilibrium was achieved.

\[ W_r = \frac{(\Delta p V/RT - W_t/M_o)(1/M_o - 1/M_w)}{W_r} \] (9)

\[ W_w = \frac{(\Delta p V/RT - W_t/M_o)(1/M_o - 1/M_w)}{W_w} \] (10)

2) Determination of equilibria in desorption step

Highly humid air (or nitrogen) was introduced to the adsorption cell at 0°C to obtain the saturated state by water condensation in the pores of carbons. Then the mixed vapor of water and solvent at a prescribed concentration was directed into the cell, where solvent vapor was adsorbed and water was partially desorbed. The adsorption equilibria of mixed vapor were determined in the same way as described for the adsorption step.

3) Determination of liquid-phase adsorption equilibria

Activated carbon was mixed with the aqueous solution of solvent in a flask, and the flask was shaken for a week in a temperature-controlled water bath at 30°C. Amount adsorbed was determined from the
initial and final concentration of liquid. The concentration of liquid was measured by ultraviolet spectrophotometer for acetone, Abbe refractometer for methanol and Total Organic Carbon Analyser for benzene and toluene.

3. Results and Discussion

3.1 Experimental results
studied. The experimental data of adsorption equilibria for mixed vapors are listed in Table 2. The data of adsorption and desorption equilibria for solvent-water vapor mixtures are presented in Table 3. In Tables 2 and 3, \( q_0 \) and \( q_0^w \) are also listed. The data in Table 3 show that the hysteresis is more outstanding for water-insoluble solvent than for water-soluble solvent.

The equilibria obtained for liquid-phase adsorption are expressed by the Freundlich equation, namely

\[
q^* = Cx^{1/n}
\]

(11)

C and n are presented in Table 4.

### 3.2 Discussion of the assumptions

1) Assumption 1 In the region of larger amount of water vapor adsorbed, the dry surface area is small, and neglecting the adsorption of water on the dry surface does not seriously influence the predicted results. However, in the region of smaller amount of water adsorbed, the fraction of dry surface area increases and Assumption 1 may be the cause of underestimation of the amount of water vapor adsorbed.

2) Assumption 2 Dubinin et al.\(^5\) have derived an equation to express the isotherm of water vapor in the range of low concentration on activated carbon. In applying their theory to the present case, the coverage of hydrophilic sites (supposed to be caused by oxygen complexes) is given to be nearly equal to 0.04 for Shirasagi S and 0.03 for HGI-780. On the other hand, when water-soluble solvent is adsorbed, the coverage of solvent molecules adsorbed is from 0.2 to

### Table 3 Comparisons of data in adsorption step and in desorption step

<table>
<thead>
<tr>
<th>Adsorption (observed)</th>
<th>Desorption (predicted)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( q_0 )</td>
<td>( q_0^w )</td>
</tr>
<tr>
<td>Acetone-Water</td>
<td>Shirasagi S</td>
</tr>
<tr>
<td>0.908</td>
<td>23.7</td>
</tr>
<tr>
<td>0.101</td>
<td>0.161</td>
</tr>
<tr>
<td>0.305</td>
<td>0.129</td>
</tr>
<tr>
<td>0.009</td>
<td>0.122</td>
</tr>
<tr>
<td>HGI-780</td>
<td></td>
</tr>
<tr>
<td>4.493</td>
<td>25.5</td>
</tr>
<tr>
<td>0.053</td>
<td>0.267</td>
</tr>
<tr>
<td>0.391</td>
<td>0.041</td>
</tr>
<tr>
<td>0.001</td>
<td>0.015</td>
</tr>
</tbody>
</table>

### Table 4 Parameters in Freundlich equation

<table>
<thead>
<tr>
<th>Activated System</th>
<th>System</th>
<th>( C )</th>
<th>( n )</th>
<th>( x )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shirasagi S</td>
<td>Acetone-Water</td>
<td>8.67</td>
<td>1.61</td>
<td>( 10^{-4}-10^{-5} )</td>
</tr>
<tr>
<td></td>
<td>Methanol-Water</td>
<td>0.37</td>
<td>2.08</td>
<td>( 10^{-5}-3 \times 10^{-4} )</td>
</tr>
<tr>
<td></td>
<td>Benzene-Water</td>
<td>8.47</td>
<td>2.88</td>
<td>( 10^{-5}-10^{-4} )</td>
</tr>
<tr>
<td></td>
<td>Toluene-Water</td>
<td>1.20</td>
<td>7.78</td>
<td>( 10^{-5}-10^{-4} )</td>
</tr>
<tr>
<td></td>
<td>Acetone-Water</td>
<td>1.60</td>
<td>2.43</td>
<td>( 10^{-1}-10^{-5} )</td>
</tr>
<tr>
<td></td>
<td>Methanol-Water</td>
<td>0.35</td>
<td>1.59</td>
<td>( 10^{-2}-3 \times 10^{-1} )</td>
</tr>
</tbody>
</table>

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0.9 and is far larger than the coverage of hydrophilic sites. These solvent molecules adsorbed act as hydrophilic sites, so Assumption 2 is acceptable.

3) Assumption 3 To check the validity of Assumption 3, an adsorption experiment of mixed vapor on activated carbon saturated beforehand with benzene was carried out. The experimental conditions and results were as follows. The concentration of benzene in the gas phase was 208.3 ppm and the relative humidity was 0.760 at 30°C. The amount adsorbed was 0.096 g/g for benzene and 0.237 g/g for water. On the other hand, the experimental results using activated carbon which was not previously saturated with benzene were 0.105 g/g for benzene and 0.233 g/g for water. The agreement of the two sets of results indicates that the number of hydrophilic and hydrophobic sites is not affected by adsorption of water-insoluble solvent. Thus, water-insoluble solvent is adsorbed preferentially on hydrophobic sites of activated carbon, and the molecules adsorbed behave hydrophobically. On the other hand, water is adsorbed only on hydrophilic sites. Therefore the validity of Assumption 3 is certified, at least for the conditions examined.

3. 3 Consideration of amount of solvent in condensed phase
In adsorption of saturated mixed vapor, \( r \) in Eq. (8) is infinitesimally large and it can be supposed that the all pores in activated carbon are filled up with the condensed phase. As dry surface does not exist, the amount of solvent adsorbed is given as the sum of \( q_o \) and \( q_z \). The comparison of \( q_o \) obtained from the adsorption experiment of saturated mixed vapor and the adsorbed amount given from the liquid-phase isotherm corresponding to the concentration of liquid phase in equilibrium with the mixed vapor is given in Fig. 7. The agreement of these values verifies the model proposed here.

3. 4 Comparisons of predicted and observed equilibriums
To predict the adsorption equilibria listed in Tables 2 and 3, the adsorption and desorption isotherms of water (Fig. 2), the adsorption isotherms of solvent (Figs. 5 and 6) and the isothermal vapor-liquid equilibria presented in the literature are used. The results predicted by the present method are listed in Tables 2 and 3, and comparisons of the predicted and observed values are shown in Figs. 8, 9 and 10.
The standard deviation between observed and predicted values is about 15% except for the data on very small amount adsorbed. Figures 8, 9 and 10 indicate that the proposed method is adequate for industrial design calculations of adsorption process.

Conclusion

A new method is proposed to predict the influence of humidity on adsorption equilibria of solvent vapors. The necessary data for prediction are the single-component isotherms, the liquid-phase isotherms and the isothermal vapor-liquid equilibria.

The predicted results were compared with experimental results for two kinds of activated carbons of different pore size distributions for water-soluble solvents (methanol and acetone) and water-insoluble solvents (benzene and toluene). The good agreement between predicted and observed results shows the validity of the proposed method.

Appendix

The composition \( x' \) of capillary condensed phase in equilibrium with a given composition and total pressure of vapor phase deviates from the composition \( x \) of the solution having a plane surface\(^2\). The Kelvin equation for component \( i \) is given as Eq. (A-1).

\[
\ln p'_{i}/p_i = -2\gamma_i V_{i} \cos \alpha/(rRT) \quad (A-1)
\]

where \( p'_{i} \) is the vapor pressure of the pure liquid in the pore. The partial pressure and composition of the solution which has a curvature is related by

\[
p_i = \gamma_i x'_i p'_{i} \quad (A-2)
\]

where \( \gamma_i \) is the activity coefficient of component \( i \).

\[
\sum_{i=1}^{n} p_i = p_T \quad (A-3)
\]

\[
\sum_{i=1}^{n} x'_i = 1 \quad (A-4)
\]

The composition of capillary condensed phase can be determined from Eqs. (8), (A-1) and (A-2) so as to satisfy Eq. (A-4), if the activity coefficients remain constant as the curvature varies. In the present work the difference of \( x \) and \( x' \) is less than a few percent.

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Nomenclature

\[
\begin{align*}
C & = \text{constant} \\
M & = \text{molecular weight} \\
n & = \text{Freundlich constant} \\
p & = \text{pressure} \quad [\text{mmHg}, \text{ppm}] \\
p_r & = \text{relative pressure (relative humidity)} \\
p_s & = \text{saturated vapor pressure} \quad [\text{mmHg}] \\
p_v & = \text{vapor pressure of pure liquid} \\
p_T & = \text{total pressure} \\
p_T' & = \text{total pressure at concentration of condensed phase} \quad [\text{mmHg}] \\
qu & = \text{amount adsorbed} \quad [\text{g/g-carbon}] \\
R & = \text{gas constant} \quad [\text{cc·mmHg/mol·°K}] \\
r & = \text{pore radius} \quad [\text{nm}, \text{Å}] \\
S & = \text{surface area} \quad [\text{m}^2/\text{g-carbon}] \\
S_f & = \text{surface area of wet surface} \quad [\text{m}^2/\text{g-carbon}] \\
S_D & = \text{surface area of dry surface} \quad [\text{m}^2/\text{g-carbon}] \\
S_T & = \text{total surface area} \quad [\text{m}^2/\text{g-carbon}] \\
T & = \text{temperature} \quad [°K] \\
V & = \text{volume} \quad [\text{cc}] \\
V_c & = \text{volume of condensed phase} \quad [\text{cc/g-carbon}] \\
V_w & = \text{molar volume of liquid} \quad [\text{cc/liquid/mol}] \\
W & = \text{amount of adsorbate} \quad [\text{g}] \\
w & = \text{volume fraction} \\
x & = \text{mole fraction in liquid phase} \\
x' & = \text{mole fraction in capillary condensed phase} \\
\alpha & = \text{contact angle} \quad [°] \\
\gamma & = \text{activity coefficient} \\
\rho & = \text{density} \quad [\text{g/cc}] \\
\sigma & = \text{surface tension} \quad [\text{dyne/cm}] \\
\end{align*}
\]

\(<\text{Subscripts}>\)

\begin{align*}
i & = \text{species in multicomponent system} \\
\text{solvent} & \\
t & = \text{total of water and solvent} \\
\text{water} & \\
1 & = \text{adsorption on dry surface} \\
2 & = \text{dissolution into condensed phase} \\
3 & = \text{liquid-phase adsorption onto wet surface} \\
\end{align*}

\(<\text{Superscripts}>\)

\begin{align*}
0 & = \text{pure component} \\
' & = \text{capillary condensed phase} \\
\end{align*}

Literature Cited


(A part of this paper was presented at the 10th Autumn Meeting, SCEJ, Nagoya (October, 1976).)