Adsorption from Binary Gas Mixtures—Applicability of BET & Ideal Adsorbed Solution Models

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Mixed BET and ideal adsorbed solution models have been applied to adsorption of binary gas mixtures on silica surfaces at —184°C. Both the models have been found to predict the adsorption equilibria satisfactorily for argon-oxygen mixtures. For nitrogen-carbon monoxide mixtures the predictions are poor, while for nitrogen-argon mixtures, the validity of the models is better in the multilayer region. The applicability of these models has been discussed and causes for the deviations have been analysed.

Among the current models for characterizing binary and multicomponent adsorption equilibria, the Ideal Adsorbed Solution Theory (IAST) of Prausnitz and Myers has been the most successful one. Nevertheless, the mixed BET and Langmuir theories continue to have certain advantages over the rest of the models because, in spite of the apparent complexity, the parameters required for their application, namely the BET and Langmuir constants, are easily evaluated from the single gas data. There is a tendency to overlook these models because of the tedious calculations involved. The present work critically examines the BET and IAST models and highlights the advantages of these models with a view to evaluating the scope of their application.

Theory

BET equation for mixture adsorption — The BET model for multilayer adsorption of pure gases was extended to mixtures by Hill who considered the applicability of the mixed BET equation to be a rigorous test for the basic assumptions of the original theory. A statistical mechanical extension of BET theory to mixtures was given by Bussey the final form of which was

\[
\theta_n = \frac{V_1}{V_m} = \frac{t x_1(1 + \tau_1 - 1)(1 - S)}{(1 - S)(1 + (1 - 1)S)}
\]

where, \(V_1\) is the volume adsorbed, \(V_m\) is the monolayer volume and \(x_1\) is the relative pressure of component 1. Besides,

\[
t = \frac{C_1 x_1 + C_2 x_2}{S} \quad (2)
\]

\[
S = x_1 + x_2 \quad (3)
\]

\[
\tau_1 = \frac{C_1}{t} \quad (4)
\]

where \(C_1\) and \(C_2\) are the BET constants for the two components derived from the single gas data. Equation 1 can be rewritten and simplified to obtain an expression for the adsorbed phase and gas phase compositions in terms of the mole fraction of component 1 in adsorbed phase \(X_1\) and gas phase \(Y_1\) respectively:

\[
X_1 = \frac{V_1}{V_1 + V_2} = \frac{1}{C_2 + (C_1 - C_2)x_1 V_m p_1^0 p_2 \left(1 - Y_1\right)} \left(\frac{1 - S}{C_1 - (C_1 - C_2)x_2 V_m p_2^0 \left(1 - Y_1\right)}\right) \quad (5)
\]

The Ideal Adsorbed Solution Theory (IAST) — The thermodynamic model of Myers and Prausnitz expresses the binary adsorption equilibria in the form,

\[
X_1 = \frac{p - p_1^0}{p_1^0 - p_2^0} \quad (6)
\]

and

\[
Y_1 = \frac{p_2^0 X_1}{p} \quad (7)
\]

where \(p\), \(p_1^0\), and \(p_2^0\) are the equilibrium pressures of mixture and pure components 1 and 2 respectively at the spreading pressure of the adsorbed phase \(\pi\) which is defined by,

\[
\frac{\pi A}{RT} = \int_0^p \frac{n}{p} \, dp \quad (8)
\]

The first step in applying the IAST model consists of plotting the \(\pi A/RT\) versus \(p\) curves for the pure components from their adsorption data. The integral in Eq. 8 is generally evaluated graphically or ana-
lytically or by a combination of both the techniques. Having obtained the $\pi A/RT-p$ curves, $X$ and $Y$ values can be computed at different values of spreading pressure.

Materials and Methods

A hydroxylated and a dehydroxylated variety of silica gel were used as adsorbents in the present study. Three sets of binary mixtures were studied, namely, argon-oxygen, nitrogen-carbon monoxide and argon-nitrogen. The choice of the gases was governed by the fact that the argon-oxygen pair has very close molecular properties, while nitrogen and carbon monoxide have polar characteristics. The argon-nitrogen pair was chosen specifically because argon is a totally non-polar molecule but nitrogen has a strong quadrupole. The different types of interaction of these molecules with the surface are expected to influence the applicability of different models to the adsorption equilibria.

Silica-1 was a hydroxylated silica gel and Silica 2 was a dehydroxylated variety, which was obtained by heating Silica 1 at 1000°C for 24 hr. All the adsorption experiments were conducted at -184°C. Prior to each experiment the adsorbent samples were degassed at 300°C for 3 hr at $10^{-5}$ torr. The description of apparatus and experimental procedure have been given elsewhere.

Results and Discussion

The experimental results on argon-oxygen and nitrogen-carbon monoxide adsorption have been presented earlier and the same have been utilised in the present analysis. The data on argon-nitrogen mixture adsorption on Silica-2 have been given in Table 1. In the Ar-O$_2$ and N$_2$-CO mixtures, O$_2$ and CO respectively are selectively adsorbed and the selectivity is nearly independent of total pressure. On the contrary in the case of Ar-N$_2$ mixtures at pressure of nearly 90 torr, both the components are adsorbed equally while with the increase in total pressure argon is selectively adsorbed.

Application of mixed BET equation — Fig. 1 gives the X-Y diagrams for the adsorption of Ar-O$_2$ mixture on Silica-1 and Silica-2 as calculated by Eq. 5. The single gas data used in the calculation are given in Table 2. The continuous lines in Fig. 1 were obtained by calculation while the circles represent the experimental data. A similar comparison has been made in Fig. 2 between the experimental and calculated phase diagrams for N$_2$-CO and Ar-N$_2$ mixtures on Silica-2. It is to be noted that except for Ar-N$_2$ mixtures, a single, unique X-Y diagram is predicted for a given system for all total pressures. For Ar-N$_2$ mixtures only, the predicted X-Y diagram depends on the total pressure.

It can be seen from Figs 1 and 2 that for Ar-O$_2$ mixtures, there is a good agreement between predicted and experimental values while the deviation is large for N$_2$-CO mixtures. For Ar-N$_2$ mixtures, considerable deviation is observed in the lower pressure region (~90 torr) but a better agreement is seen at higher pressures. In other words, BET theory is not obeyed in the submonolayer region.

### Table 1 — Adsorption from Argon-Nitrogen Mixtures on Silica-2

<table>
<thead>
<tr>
<th>Mol fr of Ar in gas phase</th>
<th>Mol fr of Ar in adsorbed phase</th>
<th>Total pressure (torr)</th>
<th>Total adsorption (cc STP)/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.940</td>
<td>0.938</td>
<td>84.2</td>
<td>55.2</td>
</tr>
<tr>
<td>0.850</td>
<td>0.851</td>
<td>91.2</td>
<td>54.7</td>
</tr>
<tr>
<td>0.720</td>
<td>0.733</td>
<td>90.7</td>
<td>51.0</td>
</tr>
<tr>
<td>0.662</td>
<td>0.678</td>
<td>84.3</td>
<td>50.0</td>
</tr>
<tr>
<td>0.405</td>
<td>0.444</td>
<td>100.0</td>
<td>49.0</td>
</tr>
<tr>
<td>0.405</td>
<td>0.514</td>
<td>214.0</td>
<td>60.7</td>
</tr>
<tr>
<td>0.457</td>
<td>0.580</td>
<td>259.0</td>
<td>67.9</td>
</tr>
<tr>
<td>0.590</td>
<td>0.696</td>
<td>243.4</td>
<td>72.0</td>
</tr>
<tr>
<td>0.280</td>
<td>0.399</td>
<td>340.8</td>
<td>72.0</td>
</tr>
<tr>
<td>0.345</td>
<td>0.489</td>
<td>414.0</td>
<td>80.8</td>
</tr>
<tr>
<td>0.380</td>
<td>0.520</td>
<td>356.0</td>
<td>77.5</td>
</tr>
<tr>
<td>0.575</td>
<td>0.702</td>
<td>376.8</td>
<td>87.6</td>
</tr>
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### Table 2 — Adsorption from Single Gases on Silica 1 and Silica 2

<table>
<thead>
<tr>
<th>Adsorbate</th>
<th>Monolayer volume (cc STP/g)</th>
<th>BET surface area (m$^2$/g)</th>
<th>BET constant C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>89.5</td>
<td>345</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>(66.5)</td>
<td>(225)</td>
<td>(30)</td>
</tr>
<tr>
<td>O$_2$</td>
<td>100.5</td>
<td>375</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>(70.4)</td>
<td>(265)</td>
<td>(30)</td>
</tr>
<tr>
<td>N$_2$</td>
<td>91.2</td>
<td>410</td>
<td>160</td>
</tr>
<tr>
<td>CO</td>
<td>97.1</td>
<td>443</td>
<td>190</td>
</tr>
<tr>
<td></td>
<td>(59.1)</td>
<td>(270)</td>
<td>(80)</td>
</tr>
</tbody>
</table>

*Data from ref. 9.
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Fig. 2 — BET prediction for argon-nitrogen and nitrogen-carbon monoxide mixtures on Silica-1.

\( \theta \) 90 torr \( \sim 0.75 \) while the deviation is negligible in the multilayer region \( \theta \) 250 torr \( \sim 1.3 \).

**Application of IAST to mixture adsorption** — Figures 3 and 4 give a comparison between the calculated and observed X-Y diagrams for different systems. In general the agreement between the two is satisfactory in the case of Ar-O\(_2\) and Ar-N\(_2\) mixtures. However, in the case of N\(_2\)-CO mixtures large deviation is observed and the prediction by the theory is only qualitative for this system. It is interesting to note that as in the case of mixed BET model, IAST also predicts single and unique X-Y diagrams for Ar-O\(_2\) and N\(_2\)-CO mixtures while a pressure dependent diagram is predicted for Ar-N\(_2\) mixtures.

Myers\(^{19}\) has examined the validity of IAST in the multilayer region in the case of oxygen-nitrogen mixtures and has observed that calculated values showed about 20% deviation from the experiment. Based on this data he concluded that IAST was not applicable in the multimolecular region though there were doubts regarding the experimental accuracy of his results. Kabel and Henson\(^{21}\) thought it unlikely that IAST would be obeyed in the multilayer region. It is seen in the present work that the formation of the multilayer is not a limitation for the theory. For instance in Fig. 3 (curve 2) the majority of points occur in the multilayer region and some of the points are at the coverages \( \sim 2 \). Similarly in the case of IAST prediction for argon-nitrogen adsorption (Fig. 4) it can be seen that the IAST model is well obeyed at pressures of 350 torr where the average coverage is nearly 1.5 monolayers. In fact the validity is better in the multilayer than in the sub-monolayer region.

**Applicability of IAST and BET models to the adsorption from mixtures of gases** — From the foregoing discussion it is seen that both IAST and BET theory are satisfactorily obeyed by the Ar-O\(_2\)-silica gel system. But the N\(_2\)-CO-silica systems show large deviations from both theories. In the case of N\(_2\)-Ar-Silica-2 system, however, BET and IAST models are obeyed well only in the multilayer region. The deviation in the case of IAST, however, is less than 10%. Thus it is evident that the BET model can be adopted to calculate adsorption from mixtures in a number of cases, the applicability being determined by the type of system; for all the multimolecular adsorption systems the applicability of BET model is only marginally inferior to that of IAST.

It is informative to investigate the deviations observed from the BET and IAST predictions. In the case of the mixed BET equation the deviation
can arise due to (i) possible inapplicability of the BET postulates in the case of mixture adsorption (ii) any inaccuracies in the value of the BET constants $V_m$ and $C$, calculated from the single gas data and (iii) inapplicability of the assumptions made in extending the theory of single gases to mixtures i.e. the Raoult’s law and the equality of the molecular sizes of the gases. However, the mixed BET equation has been obeyed well in the case of oxygen-argon mixtures thus ruling out (i) as the cause of the deviations. Further, the gases used have fairly close molecular sizes and the values of $V_m$ calculated from BET are generally correct. Thus the only source of errors could be the assumption of the validity of Raoult’s law and the accuracy of the constant $C$ as calculated from the BET plot. Again, in the case of IAST, the source of deviation can be only the incorrectness of the spreading pressure and the invalidity of Raoult’s law to adsorbed phase-gas phase equilibrium for multicomponent systems.

The fact that both IAST and BET models hold good for Ar-O$_2$ mixtures while large deviations are found in the case of N$_2$-CO mixtures shows that there is an inherent weakness in the applicability of these models for multicomponent adsorption. The only significant differences between the two pairs are in modes of interaction of the components. In the argon-oxygen pair the individual gases interact through mainly dispersion forces, whereas nitrogen and carbon monoxide have residual electric moments through which the two gases interact. During the adsorption from mixtures the interaction between dissimilar molecules (A-B interactions$^{15}$) in the adsorbed phase is the additional component of the total energetics. The parameters derived from single gas data (constant $C$ in the case of BET and spreading pressure in the case of IAST) characterize the energetics to a good degree of approximation when the adsorbates involved have similar molecular properties such as in the case of Ar, O$_2$ and hydrocarbon mixtures. The majority of systems to which IAST, isotherm equations, and other models have been successfully employed belong to this category$^{13,14}$. However, when the molecular properties are significantly different as in the case of N$_2$ and CO, the values of $C$ or spreading pressure are no longer adequate to describe the energetics of mixture adsorption since the A-B interaction present in the mixed phase is very different than the A-A and B-B interactions present in the single gas adsorption. As a consequence the IAST or other models do not satisfactorily predict adsorption equilibria in such systems. The lateral interaction between the unlike molecules will be less significant at low surface coverages and in such cases these models can be expected to be obeyed. This is perhaps the reason for the validity of IAST for N$_2$-O$_2$ mixtures on silica gel at 0°C as pointed out by Myers$^{10}$.

In the case of the adsorption from N$_2$-Ar mixtures on silica gel at -184°C, the monolayer consists of nearly equal number of molecules of the two gases so that the A-B interaction becomes significant. But in the higher layers, mainly argon is adsorbed because of its lower saturation vapour pressure. Hence it is to be expected that IAST will be obeyed better in the higher layers than in the monolayer.

Thus, in the theoretical models for characterizing multicomponent adsorption equilibria based on single component data, an inherent weakness is the lack of energy parameter representing the lateral interaction between the dissimilar molecules (A-B interactions) in the adsorbed phase. If and when the A-B interactions are comparable in nature and magnitude to A-A and B-B interactions, as in the case of mixtures of nonpolar molecules, these models can predict the equilibria fairly accurately. Any deviations from the prediction in such cases essentially arise out of errors in the evaluation of the pure component parameters, namely spreading pressure in IAST and constant $C$ in BET equation. On the other hand if the molecules concerned have widely differing physical characteristics, predictions based on single gas data will not be satisfactory in spite of any refinements of the models or improvisation in the method of application.

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References