Abstract: - Data of adsorption isotherm of propane on activated carbon (AC), molecular sieve carbon (MSC), MS13X and MS5A at 303K, 328K and 353K are acquired using constant volumetric method. Isosteric heats can be obtained indirectly from the isotherms using the Clausius-Clapeyron equation. The data is then fitted to several conventional and new models using regression method which is done at all three temperatures simultaneously. A new version of Clausius-Clapeyron equation is used to validate the range of temperatures of the isotherms in order to use it to obtain the isosteric heats. Models are fitted into both the adsorption isotherms and isosteric heats of adsorption data. While each model has only marginal differences between each other for the goodness-of-fit for the isotherms are, the representation of isosteric heats differentiate the models from each other.

Keyword: Adsorption, isotherm, VOCs, isosteric heats, equilibrium models

1. Introduction

Accurate pure and mixture adsorption equilibria, isosteric heats and kinetics are among the important input variables for design and optimisation of pressure swing and thermal swing adsorption processes for separation and purification of gases and gaseous mixtures [1]. Many mathematical models have been derived and developed to correlate adsorption isotherms. Service life, or adsorbent bed breakthrough, is estimated using combined parameters from the isotherm and rate (kinetic) equations, environment conditions and bed design. Isosteric heat is also important in understanding the adsorption equilibria. Ahmadpour et al.[2] have stressed that in modelling of adsorption processes, mass and heat balances that are set up must have proper equations for the correct description of adsorption equilibria as well as heat of adsorption.
2. Experimental Procedures and Results

The adsorption isotherms are obtained via volumetric method using the automatic surface area analyser equipment ASAP2000 by Micromeritics Corp. The adsorbate is propane and the adsorbents studied are activated carbon (charcoal), molecular sieve carbon, molecular sieve 13X (MS13X) and molecular sieve 5A (MS5A) at temperatures 303K, 328K and 353K. Details on the experimental methods can be found in Islina [3]. Figures 1 and 2 show the isotherms obtained are of Type 1.

![FIGURE 1 Isotherms for Propane-AC systems (left) and Propane-MSC systems(right)](image1)

![FIGURE 2 Isotherms for Propane-MS5A systems (left) and Propane-MS13X systems (right)](image2)

The linear region of unit slope is the Henry’s law region [4]. Isosteric heats of adsorption at zero coverage obtained from experimental data are listed in Table 1. Unfortunately, at very low pressures, the data points at 303K for activated charcoal, molecular sieve 5A and molecular sieve carbon do not have linear slope of unity (as seen from the overlapping of isotherms in Figure 1 in low pressure region), indicating that there are some errors in the experiments. Hence, the heats of adsorption of these propane systems have to be the Henry’s constant at 328K and 353K.

Clausius-Clapeyron equation, derived from the two-phase equilibrium theory, has been widely used in adsorption studies. Among them are the determinations of isosteric heats obtained experimentally from adsorption isotherms and from equilibrium models such as Langmuir equation. Jeong et al. [5] proposes a different approach to estimate a family of isotherms within a reasonable temperature range. From Clausius-Clapeyron equation,

\[
q_{st} = RT^2 \left[ \frac{\partial \ln P}{\partial T} \right]_N
\]

(1)

For isotherms measured at two temperatures, the equation becomes

\[
q_{st} = R \left[ \ln \frac{P_1 - \ln P_2}{1/T_2 - 1/T_1} \right]_N
\]

(2)
where $q_{st}$ is isosteric heat, $P_1$ and $P_2$ are the equilibrium pressures measured at temperatures $T_1$ and $T_2$ respectively, at the constant amount adsorbed, $N$. Manipulating this equation, the equation becomes

$$P = \exp \left[ \ln \frac{P_1 - \ln P_2}{1/T_2 - 1/T_1} + \ln P_2 \right]$$

(3)

Besides the prediction of an isotherm, this method can also be used to verify that the isotherms obtained are within the range of using the Clausius-Clapeyron equation. This is important since the isosteric heats from the models are calculated using this equation and also the isosteric heats obtained directly from the data. It is recommended that at least three isotherms are needed to perform the validation step. Two isotherms are possible, however, the isotherm obtained should be of a good shape to conclude that the isotherms are within the Clausius-Clapeyron range of temperatures.

Data shown for this validation is taken from Islina [3] for propane on MS5A at 303K, 328K and 353K. Plots in Figure 3 show the agreement between the experimental data and the isotherms obtained from equation (3) are excellent.

FIGURE 3 Adsorption isotherms of propane-MS5A at 303K (above left), 328K (above right) and 353K (below center)

The ability to agree with experimental data shows that the use of Clausius-Clapeyron equation is valid. Isotherms at temperature far higher or lower than the temperature range are very erroneous.

3. Isosteric heats of adsorption

After determining that the isotherms studied are within the valid region of using the Clausius-Clapeyron equation, the isosteric heats are obtained directly from the adsorption isosteres and indirectly from the adsorption isotherms.
Figure 4 shows the isosteric heats of the propane adsorption systems.

4. Correlation of Adsorption Isotherms and Isosteric Heats

A survey of equilibrium models has been done which includes conventional models and several newly developed ones [3]. It is found that modified version of Toth equation along with the conventional one have good potentials in correlating the isotherms of Type 1 as well as the isosteric heats. Details of the models are given in the work of Islina[3]. Amongst the models under survey are Langmuir[6], Langmuir-Freundlich, Dual Langmuir (DL and DLc), Toth and Unilan. New ones include Keller-Staudt-Toth[7], Modified Toth and Multispace Adsorption model which are presented in Table 1.

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>Henry’s constant, mmol g⁻¹ kPa⁻¹</th>
<th>Heat of Adsorption, kJ mole⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>303 K</td>
<td>328</td>
<td>353</td>
</tr>
<tr>
<td>Activated</td>
<td>-</td>
<td>36.9000</td>
</tr>
<tr>
<td>Charcoal</td>
<td>0.7</td>
<td>07</td>
</tr>
<tr>
<td>Molecular</td>
<td>-</td>
<td>2.82</td>
</tr>
<tr>
<td>13X</td>
<td>0.6</td>
<td>25.7812</td>
</tr>
<tr>
<td>Molecular</td>
<td>0.9</td>
<td>32.2628</td>
</tr>
<tr>
<td>5A</td>
<td>0.9</td>
<td>31.2489</td>
</tr>
</tbody>
</table>

All models are dependent of temperature. Temperature correlations are in the $q_s$ (or $a$), $b$ (or $K$) terms in the equations. Unilan differ from Unilan 2 by the temperature dependence of the heterogeneity factor $s$ in Unilan 2. Toth and Toth 2 differ from each other by the temperature dependence of the parameter $t$ in Toth 2.

Toth equation:

$$q_s = \frac{bP}{1 + (bP)^t}$$  \hspace{1cm} (4)

Unilan equation:

$$q_s = \frac{1}{2s} \ln \left( \frac{1 + be^s P}{1 + be^{-s} P} \right)$$  \hspace{1cm} (5)
Dual Langmuir equation:

\[ q = q_{s1} \frac{b_1 P}{1 + b_1 P} + q_{s2} \frac{b_2 P}{1 + b_2 P} \]  

(6)

Dual Langmuir can also be taken into two forms; one with the saturation capacities \( q_s \) to be temperature dependent (DL) whereas the latter is with constant saturation capacities (DLc).

**Model Correlation Results and Discussions**

All the equilibrium models are fitted into both the isotherms and the isosteric heat plots. Below figures show the best three models that describe the isosteric heats. The isotherm correlations are not shown here since they show only marginal differences between each other. All three models correlate well with the adsorption isotherms of propane.

For propane-AC adsorption, it can be seen from Figure 6 that all equilibrium models cannot predict the isosteric heats well. Only Unilan 2 predicts roughly the shape of the isosteric heat, and it under-predicts the heats. The heat of adsorption from Henry’s constants is 36.90 kJ/mol whereas the heat from the plot below is 34.0224 kJ/mol (at loading = 0.001 mmol/g) and the difference is about 8.45%. Other models have different descriptions, with Toth 2 increases at higher pressure whereas KST have a maximum point at loading 0.3 mmol/g and decreases slowly as the loading increases.

For propane-MSC, the isosteric heats at very low loadings are generally lower than that determined by the Henry’s constants. Only Unilan is quite closely conform to the data, with the heat of adsorption at loading 21.1481 kJ/mol as opposed to 25.7812 kJ/mol which is determined from Henry’s constants, a difference of 21.9%. Isosteric heats at very low loadings cannot be determined for Langmuir-Freundlich equation since as the loading approaches zero, the isosteric heat approaches either infinity or negative infinity (not shown). This may be due to the fact that Langmuir-Freundlich does not have the correct Henry’s law limit.

One of the reasons to explain the inability to predict the heat of adsorption is that the deviation of model from experimental data at low pressures. High residuals (the difference between the values from the model and the amount adsorbed in reality) at very low amount adsorbed can be a hindrance to the accuracy in predicting heats of adsorption. In contrast to AC and MSC systems, the models describing the isotherms of propane-MS13X can fit quite well in the isosteric plots as well. The heat of adsorption from Henry’s constant is 32.2628 kJ/mol, and the heats predicted from DLc is 30.8854 kJ/mol and from MSAMMT is 30.0240 kJ/mol (at loading 0.001 mmol/g), difference of ~7.5%. The heat of adsorption is a little under-predicted but from then onwards the isosteric heats from MSAMMT and DLc follow the path from experimental data.

Isosteric heats from models for propane-MS5A systems go through a maximum point at high-pressure region except for DLc model. DLc model represent the isosteric heat quite well, with very small difference in heat of adsorption \( Q_{Henry} = 31.2489 \text{ kJ/mol and } Q_{DLc} = 31.2088 \).
kJ/mol) but increase above the heats from data at loadings more than 1.5 mmol/g.

Thus, decision can be made to choose the right model for the equilibrium systems. If the models cannot describe the isosteric heats very well, hence the choice has to be based on the best-fitted ones to the adsorption isotherms and the ones can be assumed to closely conform to the isosteric heats. Unilan 2 and Toth 2 are chosen to represent propane-AC adsorption equilibria. In propane-MSC adsorption, Unilan is chosen along with MSAMMT model. For propane-MS13X systems, DLc and MSAMMT seem to be the best choice since they are proven to be more superior in correlating both the isotherms as well as the isosteric heats. DLc and DL are chosen to represent the propane-MS5A systems.

4. Conclusion

All model compared can correctly describe the propane adsorption equilibria. However, the correlation of isosteric heats differ much between these models. MSAMMT and KST models proved to be superior in some systems and can compete with conventional models. An equation based on Clausius-Clapeyron equation has been used to verify that the isotherms are in the range of Clausius-Clapeyron usage.

References: