Heat of adsorption and adsorbed phase specific heat capacity of methane/activated carbon system

Kazi Afzalur Rahman\textsuperscript{a,*}, Wai Soong Loh\textsuperscript{b}, Kim Choon Ng\textsuperscript{b}

\textsuperscript{a}Department of Mechanical Engineering, Chittagong University of Engineering & Technology, Chittagong 4349, Bangladesh
\textsuperscript{b}Department of Mechanical Engineering, National University of Singapore, 9 Engineering Drive 1, Singapore 117576, Singapore

Abstract

This study describes the thermodynamic formulations for the heat of adsorption and the adsorbed phase specific heat capacity from the rigor of classical thermodynamics with the involvement of adsorption parameters. The abovementioned thermodynamic quantities are evaluated from the equilibrium uptakes for adsorption of methane onto different types of activated carbon and found to be strongly dependent on the adsorption parameters along with the pressure and temperature. The adsorption uptake data of methane/Maxsorb III pair for temperatures both in sub- and supercritical regions are also used in the property evaluations and it is observed that the quantities vary with temperature and the trend is opposite between the sub- and supercritical regions.

Keywords: Heat of adsorption; Specific heat capacity; Adsorption parameters; Methane; Activated carbon.

Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>Adsorbate surface loading (g/g)</td>
</tr>
<tr>
<td>(C_0)</td>
<td>Maximum specific mass of adsorption (g/g)</td>
</tr>
<tr>
<td>(c_p)</td>
<td>Specific heat capacity (kJ/kg K)</td>
</tr>
<tr>
<td>E</td>
<td>Characteristics energy (J/mol)</td>
</tr>
<tr>
<td>(H_{ads})</td>
<td>Heat of adsorption (kJ/kg)</td>
</tr>
<tr>
<td>h</td>
<td>Enthalpy (kJ/kg)</td>
</tr>
<tr>
<td>(h_{fg})</td>
<td>Latent heat of evaporation (kJ/kg)</td>
</tr>
<tr>
<td>n</td>
<td>Heterogeneity parameter (-)</td>
</tr>
<tr>
<td>P</td>
<td>Pressure (bar)</td>
</tr>
<tr>
<td>(P_{sat})</td>
<td>Saturation pressure (bar)</td>
</tr>
<tr>
<td>R</td>
<td>Gas constant (kJ/kg K)</td>
</tr>
<tr>
<td>s</td>
<td>Entropy (kJ/kg K)</td>
</tr>
<tr>
<td>T</td>
<td>Temperature (K)</td>
</tr>
<tr>
<td>(T_b)</td>
<td>Boiling temperature (K)</td>
</tr>
<tr>
<td>(v_a)</td>
<td>Adsorbate specific volume in adsorbed phase (cm(^3)/g)</td>
</tr>
<tr>
<td>(v_b)</td>
<td>Specific volume at the boiling point (cm(^3)/g)</td>
</tr>
<tr>
<td>W</td>
<td>Volumetric adsorbate uptake (cm(^3)/g)</td>
</tr>
<tr>
<td>(W_0)</td>
<td>Limiting volumetric adsorbate uptake (cm(^3)/g)</td>
</tr>
</tbody>
</table>

* Corresponding author. Tel.: +880 31 714953; fax: +880 31 714953.
E-mail address: afzalur99@yahoo.com
1. Introduction

In adsorption process, the adsorbate molecules attract to the adsorbent surface with the existence of van der Waals forces and they accumulate in the pores of the adsorbent with phase transformation. The transformed phase of the adsorbate molecules is called as adsorbed phase which is treated as a distinguishable phase in thermodynamic viewpoint, even though the precise location of the phase boundary is uncertain [1]. The thermodynamic states of the adsorbed phase are not only function of pressure and temperature like gaseous phase but also depend on adsorbate surface loading or uptake [2,3]. Therefore, it is necessary to evaluate the thermodynamic quantities for the adsorbed phase and it is not reasonable to assume the adsorbed phase to be equal to the liquid phase or to the gaseous phase.

This article describes the theoretical framework of the heat of adsorption and the adsorbed phase specific heat capacity for an adsorbate-adsorbent pair. The thermodynamic formulations are performed from the rigor of classical thermodynamics by incorporating the adsorption equilibrium model that holds the relationship between the pressure, temperature, and the uptake for an adsorption system. The adsorbed phase specific volume is also taken into consideration in deriving the theoretical relations. The property values are derived qualitatively for adsorption of methane onto different types of activated carbon. Especially, the adsorption uptake data for the methane/Maxsorb III pair are available for a wide range of temperatures both in sub- and supercritical states and pressures up to 25 bar. These experimental uptake data are used in evaluating the abovementioned thermodynamic quantities for both the sub- and supercritical regions. The evaluated values show better estimation due to the involvement of the adsorption parameters in the theoretical formulations and also because of the consideration of adsorbed phase specific volume which was assumed to be same as the gaseous phase in a recent study by Chakraborty et al. [3].

2. Theory

2.1. Adsorption equilibrium model

The relationship between pressure, temperature and uptake of an adsorbate-adsorbent system is known as the adsorption equilibrium model. Among the adsorption equilibrium models available in the literature, the Dubinin-Astakhov (D-A) model is one of the popular isotherm model for adsorption of vapours and gases onto non-homogeneous carbonaceous solids [4]. The D-A isotherm model is used in this study to describe the adsorption equilibrium uptake for the methane/activated carbon system. The D-A model is expressed as

\[
\frac{C}{(W_0/v_a)} = \exp \left[ - \left( \frac{RT}{E} \ln \left( \frac{P_s}{P} \right) \right)^n \right]
\]

where \( C \) is the amount of uptake in g/g, \( W_0 \) is the limiting uptake of adsorption space of the adsorbent in cm\(^3\)/g, \( E \) is the characteristic energy of the adsorption system, and \( n \) is the structural heterogeneity parameter. The adsorbed phase specific volume \( (v_a) \) can be estimated from the following empirical expression proposed by Ozawa et al. [5] for high pressure gas adsorption considering the thermal expansion of the adsorbate molecules.

\[
v_a = v_b \exp \left[ \alpha (T - T_b) \right]
\]

where \( v_b \) is the specific volume of the liquid at the boiling point, \( T_b \), and \( \alpha \) is the thermal expansion coefficient of the adsorbed phase.
The saturation vapour pressure \( (P_{\text{sat}}) \) of the adsorbed phase depends on the adsorption temperature for the subcritical condition of the adsorbate and it can be determined from the following Dubinin’s method, i.e. \( P_{\text{cri}} = (T/T_{\text{cri}})^2 P_{\text{cri}} \), when the adsorption occurs above the critical point.

### 2.2. Heat of adsorption

The heat release during the adsorption process due to the change in energy level of the adsorbate molecules is known as the heat of adsorption and the Clausius-Clayperon equation has long been used for evaluation of heat of adsorption from the adsorption uptake data assuming ideal gas-phase behaviour of the adsorbate molecules in their gaseous phase [6,7].

\[
H_{\text{ads}} = RT^2 \left[ \left( \frac{\partial (\ln P)}{\partial T} \right)_C \right] \tag{3}
\]

Now invoking the D-A isotherm model in Eq. (3), an explicit expression for the heat of adsorption can be obtained which is function of adsorbate surface loading \( (C) \), adsorbed phase specific volume \( (v_a) \), thermal expansion coefficient of the adsorbed phase \( (\alpha) \), adsorption parameters \( (W_0, E, n) \) of the D-A isotherm model, saturation pressure \( (P_{\text{sat}}) \), and temperature.

\[
H_{\text{ads}} = E \left[ \ln \left( \frac{W_0}{Cv_a} \right)^{1/n} + \frac{\alpha T}{n} \ln \left( \frac{W_0}{Cv_a} \right)^{1/n} \right] + RT^2 \left( \frac{\partial \ln P_{\text{sat}}}{\partial T} \right) \tag{4}
\]

Here, the second term of the right hand side is equal to \( (2RT) \) by using the proposed expression for saturation pressure \( (P_{\text{sat}}) \) in case of supercritical state. However, when the adsorption process occurs below the critical point, this term can be replaced with the heat of vaporization \( (h_{fg}) \) and the Eq. (4) becomes

\[
H_{\text{ads}} = E \left[ \ln \left( \frac{W_0}{Cv_a} \right)^{1/n} + \frac{\alpha T}{n} \ln \left( \frac{W_0}{Cv_a} \right)^{1/n} \right] + h_{fg} \tag{5}
\]

### 2.3. Adsorbed phase specific heat capacity

Thermodynamically the adsorbed phase specific heat capacity \( (c_{p,a}) \) is defined by the temperature derivative of the differential adsorbed phase enthalpy \( (h_a) \) at constant surface loading \( (C) \) [2,3,6,8], i.e.,

\[
c_{p,a} = \frac{\partial h_a}{\partial T} \tag{6}
\]

The heat of adsorption \( (H_{\text{ads}}) \) can also be expressed as the difference between the gaseous phase enthalpy and the adsorbed phase enthalpy [6], i.e.,

\[
H_{\text{ads}} = h_g - h_a \tag{7}
\]

Thus, the adsorbed phase specific heat capacity can be re-written as

\[
c_{p,a} = \frac{\partial h_g}{\partial T} - \frac{\partial H_{\text{ads}}}{\partial T} = c_{p,g} - \frac{\partial H_{\text{ads}}}{\partial T} \tag{8}
\]

where \( c_{p,g} \) is the specific heat capacity of the gaseous phase.
Invoking the expression for $H_{\text{ads}}$ from Eq. (5) in the above Eq. (8), the $c_{p,a}$ becomes

$$c_{p,a} = c_{p,g} + \frac{\alpha^2 (1-n)}{n^2} E T \ln \left( \frac{W_0}{C V_a} \right) \frac{1-2n}{n} - \left( \frac{\partial h_{fg}}{\partial T} \right)_p$$

(9)

The second term of the right-hand side can be determined from the adsorption parameters ($W_0, E, n$) of the D-A isotherm model, adsorbed phase specific volume ($v_a$), thermal expansion coefficient for the adsorbed phase ($\alpha$), adsorbate surface loading ($C$), and temperature.

For sub-critical condition of the adsorbate, the partial term $\left( \frac{\partial h_{fg}}{\partial T} \right)_p$ can be expressed as $\left( c_{p,g} - c_{p,f} \right)$ and Eq. (9) eventually becomes

$$c_{p,a} = c_{p,f} + \frac{\alpha^2 (1-n)}{n^2} E T \ln \left( \frac{W_0}{C V_a} \right) \frac{1-2n}{n}$$

(10)

For super-critical condition of the adsorbate, the partial term $\left( \frac{\partial h_{fg}}{\partial T} \right)_p$ reduces to $(2R)$ in Eq. (9).

$$c_{p,a} = \left( \frac{\partial h_{fg}}{\partial T} \right)_p - \left( \frac{\partial H_{ads}}{\partial T} \right)_C = c_{p,g} - \left( \frac{\partial H_{ads}}{\partial T} \right)_C$$

(11)

3. Results and discussion

3.1. Adsorption Isotherms

The adsorption uptake data measured for methane/Maxsorb III pair using the volumetric technique are plotted Fig 1 for temperatures ranging from (120 to 350) K and pressures up to 25 bar. These experimental uptake data are reported by Loh et al. [9] for the temperatures in super-critical region from (278 to 350) K whilst Rahman et al. [10] has published the isotherm data for sub-cryogenic temperatures ranging from (120 to 220) K for the methane/Maxsorb III pair.

![Adsorption Uptake vs Pressure for Methane/Maxsorb III Pair](image-url)
To describe the experimental uptake data, the Dubinin-Astakhov isotherm model is used and it is found to be more appropriate for the present adsorbate-adsorbent pair due to (i) the accountability of the heterogeneity parameter and (ii) the consideration of the adsorbed phase volume correction. The expression for adsorbed phase specific volume \( v_a \) of Eq. (2) is incorporated with the D-A isotherm model and the thermal expansion coefficient \( \alpha \) of the \( v_a \) expression has kept being float to regress well the isotherm data in sequence with the study by Rahman et al. [10]. The regressed adsorption parameters are 2.193 cm\(^3\)/g, 4757.3 J/mol, 1.05 and 0.0043 K\(^{-1}\) for \( W_0, E, n, \) and \( \alpha \), respectively. The heterogeneity parameter \( n \) is very close to unity which indicates the adsorbent surface to be highly heterogeneous and thus results a lower value of characteristics energy \( E \). An average regression error of about 7 % is found for this analysis. The solid lines in Fig 1 are predicted for the same temperatures from the D-A isotherm model using the regressed parameters. It can be seen that all the predicted isotherms are within 7 % of the experimental uptake data which is reasonable when a single isotherm model is employing to fit such a wide range of uptake data. The adsorption parameters found here are important in evaluating the heat of adsorption \( H_{ads} \) and the adsorbed phase specific heat capacity \( c_{p,a} \) as function of pressure \( P \), temperature \( T \) and amount of adsorption uptake \( C \).

### 3.2. Heat of adsorption

The heat of adsorption \( H_{ads} \) values for methane/Maxsorb III pair are evaluated using Eq. (5) and plotted in Fig 2(a) and 2(b) against adsorbate surface loading \( C/C_0 \) for sub- and supercritical temperatures, respectively. It can be seen that the heat of adsorption decreases with increasing temperature in the subcritical region and the trend is opposite in the supercritical states. Again, the heat of adsorption varies with adsorbate surface loading and approaches to a limiting value when adsorption process proceeds towards the saturation uptake limit. This variation of the heat of adsorption with the adsorbate surface loading is due to the surface heterogeneity of the adsorbent. These \( H_{ads} \) values are important for thermodynamic analysis of any adsorption system. For example, the effective thermal management of ANG storage system requires precise information of heat of adsorption that generates during the charge process of the system.

![Fig. 2. Heat of adsorption \( H_{ads} \) for methane/Maxsorb III pair against adsorbate surface loading \( C/C_0 \) at (a) Sub-critical and (b) Super-critical temperatures](image)

The \( H_{ads} \) values are also evaluated for adsorption of methane onto different types of microporous activated carbons. Since the developed expression for \( H_{ads} \) requires the adsorption parameters \( (W_0, E, n, \) and \( \alpha) \) for the adsorbate-adsorbent pair, a number of activated carbons are cited from the literature those conducted experiment for the adsorption isotherms of methane. All the cited samples are microporous in surface structure and the isotherm data are in the supercritical range. The adsorption uptake data of methane on these activated carbons are taken from the respective articles and regressed with the D-A isotherm model. The adsorbent characteristics of the carbon samples and the adsorption parameters of the D-A isotherm model are summarized in Table 1. The heat of adsorption \( H_{ads} \) values are plotted in Fig 3 against the adsorbate surface loading \( C/C_0 \) at temperature of 298 K for adsorption of methane onto the activated carbon samples mentioned in Table 1. It is observed that the \( H_{ads} \) varies with adsorbate surface loading for all the samples and this variation is wider range in case of Maxsorb III than the other carbon samples.
Table 1. Parameters ($W_0$, $E$, $n$, $\alpha$) of the D-A isotherm model for adsorption of methane onto different types of activated carbon samples

<table>
<thead>
<tr>
<th>Adsorbent Samples</th>
<th>Temperature range of data measurement (K)</th>
<th>Limiting Uptake, $W_0$ (cm$^3$/g)</th>
<th>Characteristic Energy, $E$ (J/mol)</th>
<th>Heterogeneity Parameter, $n$</th>
<th>Citation$^{**}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maxsorb III</td>
<td>120 - 348</td>
<td>2.193</td>
<td>4757.3</td>
<td>1.05</td>
<td>a</td>
</tr>
<tr>
<td>AX21</td>
<td>233 - 333</td>
<td>1.08</td>
<td>5464.1</td>
<td>1.26</td>
<td>b</td>
</tr>
<tr>
<td>ACF (A-20)</td>
<td>278 - 348</td>
<td>0.717</td>
<td>6198.4</td>
<td>1.51</td>
<td>c</td>
</tr>
<tr>
<td>BPL</td>
<td>273 - 333</td>
<td>0.36</td>
<td>7040</td>
<td>1.54</td>
<td>d</td>
</tr>
<tr>
<td>Norit R1 Extra</td>
<td>273 - 323</td>
<td>0.43</td>
<td>7500</td>
<td>1.73</td>
<td>d</td>
</tr>
<tr>
<td>F30/470</td>
<td>303 - 343</td>
<td>0.389</td>
<td>7742.9</td>
<td>1.81</td>
<td>c</td>
</tr>
<tr>
<td>Chemviron</td>
<td>278 - 348</td>
<td>0.407</td>
<td>8684.1</td>
<td>1.86</td>
<td>f</td>
</tr>
<tr>
<td>Calgon AC</td>
<td>293 - 313</td>
<td>0.309</td>
<td>8955.1</td>
<td>2.41</td>
<td>g</td>
</tr>
</tbody>
</table>

*The value of $\alpha$ is 0.0025 K$^{-1}$ for all pairs except methane/Maxsorb III.

$^{**}$a. Present study; b. Zhou et al. [11]; c. Loh et al. [9] d. Himeno et al. [12]; e. Fre and De Weireld [13]; f. Author’s unpublished data; g. Choi et al. [14].

The difference of $H_{ads}$ between surface loading of $C/C_\theta=0.01$ and $C/C_\theta=0.6$, i.e. $(H_{ads})_{C/C_\theta=0.01} - (H_{ads})_{C/C_\theta=0.01}$, is calculated for each sample and Maxsorb III gives considerably larger value as shown in the inset of Fig 3. Thus, it can be said that the degree of surface heterogeneity is higher for the Maxsorb III than the other activated carbon samples. This observation has also been confirmed by Loh et al. [9] from the pore size distribution of the Maxsorb III samples by the NLDFT method.

3.3. Adsorbed phase specific heat capacity ($c_p,a$)

The adsorbed phase specific heat capacity ($c_p,a$) is function of pressure, temperature and amount of adsorbate uptake whereas the bulk specific heat capacity ($c_p$) depends only on pressure and temperature. Therefore, it is necessary to evaluate the $c_p,a$ values for thermodynamic analysis of any adsorbate-adsorbent system and Eq. (9) is developed for this purpose. In Fig 4, the adsorbed phase specific heat capacity ($c_p,a$) values are plotted against temperatures for different constant pressures. The adsorbed phase $c_p,a$ values are derived using Eq. (9) where the adsorption parameters ($W_0$, $E$, $n$, and $\alpha$) evaluated for the methane/Maxsorb III pair are used in calculating the values. Due to the availability of adsorption uptake data of methane/Maxsorb III pair for a wide range of temperatures, it is reasonable to determine the $c_p,a$ values in both the sub- and supercritical regions. In Fig 4, it can also be observed that the isobaric $c_p,a$ values are decreasing except a slight increase in the supercritical region. At pressures below 10 bar, the $c_p,a$ values start to increase immediately after the critical point. These values are also important in the study of ANG storage system to analyze its cyclic processes.
The $c_{p,a}$ values are evaluated for methane adsorption onto different activated carbon samples mentioned in Table 1 and plotted in Figs 5(a) and 5(b) for constant pressure, $P = 5$ bar and constant surface loading, $C/C_0 = 0.5$, respectively. It is observed that both the isobaric and isosteric $c_{p,a}$ values are increasing with temperatures and also in the similar trend in case of all the carbon samples. It is also observed that the $c_{p,a}$ values are dependent on the adsorption parameters and these two plots demonstrate the strong dependence on the characteristics energy ($E$) and the heterogeneity parameter ($n$). In general, the $E$ and $n$ values are larger in case of the adsorbent that have the lower degree of surface heterogeneity. Thus it can be said that the adsorbed specific heat capacity ($c_{p,a}$) of methane is relatively higher when adsorption occurs on adsorbents with heterogeneous surface.

4. Conclusions

The thermodynamic frameworks of the heat of adsorption and the adsorbed phase specific heat capacity are described in this article. The evaluated property values are found to be strongly dependent on the adsorption parameters along with the pressure and temperature. It is observed that the heat of adsorption values are decreasing with temperature in the subcritical
region and the trend is opposite in the supercritical region for the methane/Maxsorb III pair. Similarly, the adsorbed phase specific heat capacity values are observed to decreasing with temperature in the subcritical region and there is a slight increase with temperature in the supercritical region. These evaluations are significant, as they directly affect the computation of the enthalpy and entropy balances of the adsorbed phase. Such key thermodynamic quantities are essential in designing and analyzing the ANG storage system.

Acknowledgements

The authors gratefully acknowledge the financial support given by grants (R265-000-268-305) from A*STAR/MPA, Singapore and (R265-000-286-597) from King Abdullah University of Science and Technology (KAUST), KSA.

References