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Adsorption of Dichloromethane on Activated Carbon

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Adsorption is an economical option for the removal of volatile organic compounds (VOCs) from effluent streams of various industries. Its feasibility depends on the equilibrium and kinetics of the adsorption process. A conventional apparatus for the measurement of adsorption equilibria and kinetics needs dedicated equipment which may not be readily available in all laboratories. To overcome this limitation, in this work adsorption equilibrium of a VOC, namely, dichloromethane, was measured on activated carbon by a flow-through gravimetric technique using a thermogravimetric analyzer (TGA, an instrument readily available in most laboratories). Moreover, in a flow-through measurement technique the concentration of the VOC in the gas phase can be accurately controlled. The measurements were performed at three different temperatures, namely, (303.15, 318.15, and 353.15) K. The results were comparable to already available data for the adsorption of dicholoromethane on activated carbon. A virial form of isotherm best describes the isotherm behavior. The limiting enthalpy of adsorption was around −41 kJ·mol^{-1}.

1. Introduction

Volatile organic compounds (VOCs) in the urban and industrial atmosphere mainly originate from motor vehicle exhausts and other combustion processes utilizing fossil fuels, petroleum storage and distribution, solvent usage, and other industrial processes.[1−3] Several effects of VOCs are recognized, such as their contribution to stratospheric ozone depletion, tropospheric photochemical ozone formation, toxic and carcinogenic human health effects, and enhancement of the global greenhouse effect.[4−6] Bouhamra and Elkilani[7] classified VOCs into three groups: aromatics, halogenated aromatics, and halogenated aliphatics. They measured surface sorption rate constants ranging from (55.6 to 267) μm·s^{-1} depending on the chemical nature of the VOC. Their results showed that the removal rates of aliphatic and aromatic VOCs by adsorption increased if they were attached to halogen and alkyl groups, respectively.

Manjare and Ghoshal[8] attempted to establish a qualitative guideline for the selection of the appropriate adsorption technique for recovery of VOCs based on the type and concentration of the VOC, suitability of an adsorbent for a particular VOC, the extent of separation required, and different adsorption techniques available based on traditional and new advanced concepts. Once the equilibrium and kinetic data for a VOC is available, a detailed analysis as outlined by Manjare and Ghoshal[8] can then be carried out to assess the feasibility and select a suitable adsorbent.

Although measurement of adsorption equilibria can be performed through commercially available push-button type systems, it nevertheless requires dedicated apparatus. The primary objective of this work was to adapt a thermogravimetric analyzer (TGA) to perform adsorption equilibrium measurements; the dichloromethane/activated carbon system was chosen for this purpose.

Gravimetric measurements provide a direct dynamic measurement; both the equilibrium as well as the kinetics of adsorption can be readily deduced from this type of measurement.[9] In a conventional gravimetric technique, usually a pure gas is equilibrated with solid adsorbent. In the case of vapor adsorbed from a mixture with an inert gas, the concentration introduced will be different from the equilibrium concentration. Usually one needs to measure the concentration of the equilibrium mixture, as in case of binary gas mixture adsorption measurements. In such a situation, obtaining an isotherm at concentrations of interest will be difficult, if not impossible.[16] If the VOC uptake is high this problem will be more pronounced; it can however be overcome by using a flow-through type gravimetric experiment as explained elsewhere in the literature.[10] In this work we implement a flow-through gravimetric technique using a simple TGA setup.

Table 1. Physical Properties of Dichloromethane

Lennard−Jones parameter, $\sigma\cdot 10^{10}$/m	4.759
normal boiling point, T_b/K	312.65
vapor pressure of dichloromethane	$\log_{10}P/\text{kPa} = 6.20481 - 1138.91/(T/\text{K} - 41.7)$
enthalpy of vaporization/kJ·mol^{-1}	28.6

Dichloromethane is primarily used as a solvent in paint removers, a solvent for degreasing, an aerosol propellant in paints and automotive sprays, a blowing and cleaning agent in foam production, and a film processing solvent in the production of polycarbonate resins.[11−17] It has a high volatility even at room temperature. In this work it is chosen as a representative VOC to demonstrate the applicability of TGA for adsorption equilibrium measurements.

2. Material and Methods

2.1. Materials. Analytical reagent grade dichloromethane manufactured by Merck India Pvt. Ltd., Mumbai, was used in the experiments. The physical properties of interest for this compound are given in Table 1.[18] The Lennard−Jones molecular diameter for this compound is 4.759·10^{-10} m, and it will be effectively screened out of zeolites like 3A and 4A.

Activated carbon powder used in this study was obtained from Nice Chemicals Pvt. Ltd., Cochin, India. The Brunauer−Emmett−Teller (BET) surface area was measured using a

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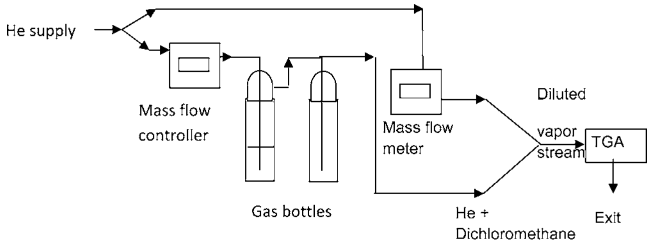

Figure 1. Schematic of experimental setup.

Beckman Coulter surface area analyzer (model: SA3100) and was about 1000 $m^2 \cdot g^{-1}$. About 18 % of total pore volume consisted of pores below 3.6 nm; 98 % of total pore volume consisted of pores below 10 nm. The particle size distribution was measured using a Malvern laser particle size analyzer (model: Mastersizer with Hydro 2000 MU unit) using methanol as the dispersion medium. The average particle size was about 24 μm.

2.2. Experimental Apparatus. The experimental setup used in the study is depicted in Figure 1. A known composition of a mixture of helium and dichloromethane vapor is sent into the TGA at a constant flow rate. The following are salient features of the experimental setup used.

a. Dichloromethane was evaporated into a stream of helium by bubbling helium (typically at about $8.33 \cdot 10^{-8}$ $m^3 \cdot s^{-1}$) through liquid dichloromethane in a gas wash bottle. Sufficient care is taken to remove any entrained liquid droplets by passing the resultant stream through polymeric resin filters.

b. The resultant stream was then diluted with a stream of pure helium to achieve a wide range of concentrations of dichloromethane.

c. The flow of helium through the gas washing bottle was controlled using a gas flow controller from Aalborg Instruments and Controls Inc. (model: GFC13). The diluent helium stream was controlled by a needle valve and the flow rate measured through a mass flow meter from MKS Instruments, Inc. (model: M10MB23CS3BN).

d. The concentration of dichloromethane in the helium stream was analyzed in a gas chromatograph with a tthermal conductivity detector (TCD), using a 3.175 mm outer diameter (OD), with a packed carbosieve column held at 398.15 K.

e. Adsorption equilibrium measurements were performed on a TGA 851 SDTA manufactured by Mettler Toledo. TGA in general has high sensitivity, relatively high vibration resistance, and a structure that permits easy replacement of the sample. Unlike most conventional gravimetric units often very small samples, that is, less than 50 mg, may be used in a TGA, a luxury that can be afforded because of its high sensitivity.

2.3. Experimental Protocol. Equilibrium experiments for dichloromethane on activated carbon were performed at three different temperatures, namely, (303.15, 318.15, and 353.15) K. The adsorbent was first regenerated by heating it at 573 K in a flow of helium for about 2 h. Complete regeneration of the sample was assumed to be achieved when the weight change was less than 0.01 mg in 30 min. In general, (1 to 2) h was needed for regeneration of the sample. Thereafter, it was cooled to the experimental temperature of interest. The sample was then equilibrated with a mixture of dichloromethane and helium, by flowing the gas mixture at the concentration of interest over the sample. Equilibrium was assumed to be achieved when the change in sample mass was less than 0.01 mg in 30 min. It was observed that usually 90 min were sufficient to reach equilibrium except at very low partial pressures, for which longer times were necessary. Successive points on the adsorption branch of the isotherm can be readily measured by simply increasing the concentration of dichloromethane. All isotherms were measured in this manner, only on the adsorption branch. To minimize accumulation of experimental error, usually equilibrium concentrations were measured for three different partial pressures (or concentrations) before the adsorbent was regenerated.

By performing a few trial runs initially, it was found that the effect of the helium flow rate on the balance signal was negligible; in any case it was ensured that the flow rate of gas mixture over the sample was always constant (at about 0.67 $\mu m^3 \cdot s^{-1}$). Moreover, unlike in the case of regular gravimetric experiments, buoyancy corrections were not required here, since the change in density of the bulk phase with the concentration of dichloromethane is negligible.

3. Equilibrium Modeling

The most commonly used model for pure component isotherms is a Langmuir model.[19]

$$\frac{n}{n_{\max}} = \frac{bP}{1 + bP} \tag{1}$$

where n is the amount adsorbed at a pressure P, $n_{\max}$ is the monolayer saturation coverage limit for the adsorbent surface, and b is related to the enthalpy of adsorption. In the original Langmuir formulation, $n_{\max}$ is independent of temperature, while the temperature dependency of n is incorporated through b via

$$b = b_0 \exp(-\Delta H_0/RT) \tag{2}$$

where b_0 is the pre-exponential factor and ΔH_0 is the enthalpy of adsorption. However as discussed later, it was not possible to obtain a good fit for experimental data using eq 2 in this work. A temperature dependency of $n_{\max}$ also had to be considered. Another convenient model is the virial isotherm[9]

$$\ln\left(\frac{P}{n}\right) = k + bn + cn^2 \tag{3}$$

k is related to Henry's constant; b and c are known as virial coefficients. The virial isotherm has a convenient polynomial form which suits analytical calculations in modeling; moreover, it is also useful to model the behavior of gas adsorption over a wide range of pressure.[9]

The Henry's constant H is defined as the slope of the isotherm at the limit of zero pressure. It is an important variable that needs to be determined with precision for any thermodynamic analysis.[9] It is related to the Langmuir constants by the relation

$$H = \lim_{P \to 0} \frac{n}{P} = bn_{\max} \tag{4}$$

The virial domain plot (left-hand side of eq 3 against n) is also useful to obtain the Henry's constant; the intercept of this plot gives the Henry's constant.[9] The Henry constant is related to the virial coefficient by

$$H = \lim_{P \to 0} \frac{n}{P} = \exp(-k) \tag{5}$$

Since H is related to the virial coefficient k through eq 5 and the temperature dependency of H is given by the van't Hoff relation, it follows that

$$k = k_0 + \frac{k_1}{T} \tag{6}$$

Similar expressions are used for the temperature dependency of other virial coefficients.

$$b = b_0 + \frac{b_1}{T} \qquad c = c_0 + \frac{c_1}{T} \tag{7}$$

In general, the enthalpy of adsorption is a function of loading on the surface and is an important variable which indicates the strength of adsorption. It can be readily obtained in terms of virial coefficients from the following relation:[9]

$$\Delta H_{\mathrm{ads}} = R(k_1 + b_1 n + c_1 n^2) \tag{8}$$

4. Results and Discussion

Equilibrium isotherms for the adsorption of dichloromethane on activated carbon at (303.15, 318.15, and 353.15) K were obtained. The adsorbed phase concentration of dichloromethane is expressed as n (moles of dichloromethane per kilogram of activated carbon), and the bulk phase concentration is expressed in terms of partial pressure of dichloromethane, P. The results are summarized in Figure 2 and Table 2. These results are comparable to earlier studies in the literature. Yun and Choi[20] measured the adsorption of dichloromethane on activated carbon (Xtrusorb-600) with a surface area of 1058 $\mathrm{m^2 \cdot g^{-1}}$. At 303 K and 320 Pa they report an equilibrium loading of 2.1 $\mathrm{mol \cdot kg^{-1}}$. Similarly, Eissmann and LeVan[21] have measured adsorption on dichloromethane on 6 × 16 mesh type BPL activated carbon (Calgon Carbon Corp.). At 298 K and 1000 Pa they report an equilibrium loading of about 3.45 $\mathrm{mol \cdot kg^{-1}}$. The values obtained in our work are slightly higher than the loading reported in both these works, probably because of the difference in the carbon samples.

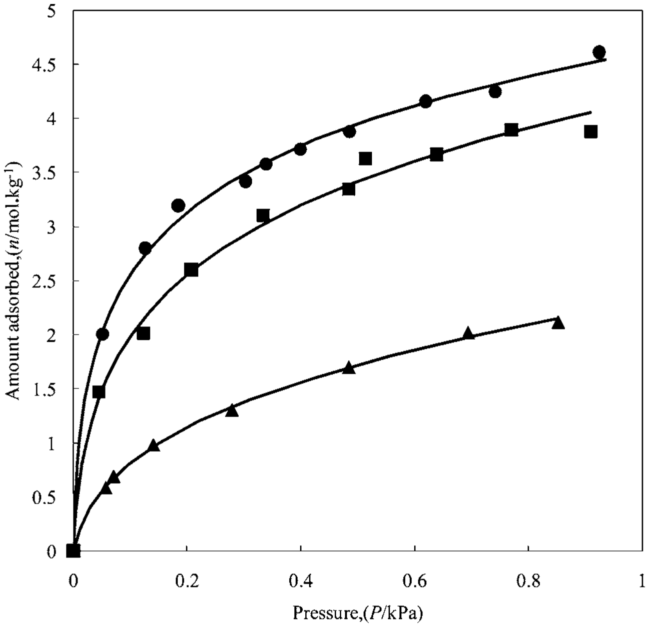

Figure 2. Isotherm of dichloromethane on activated carbon: ●, 303.15 K; ■, 318.15 K; ▲, 353.15 K. Solid lines denote predictions using virial model with parameters in Table 4.

Table 2. Adsorption on Dichloromethane on Activated Carbon

303.15 K		318.15 K		353.15 K	
P/Pa	n/mol·kg^{-1}	P/Pa	n/mol·kg^{-1}	P/Pa	n/mol·kg^{-1}
51	2.00	45	1.47	57	0.59
127	2.80	123	2.01	71	0.69
185	3.19	208	2.60	141	0.99
303	3.42	334	3.11	279	1.31
339	3.58	484	3.35	484	1.70
399	3.71	514	3.63	694	2.02
485	3.88	639	3.67		
619	4.16	770	3.89		
742	4.25	909	3.87		

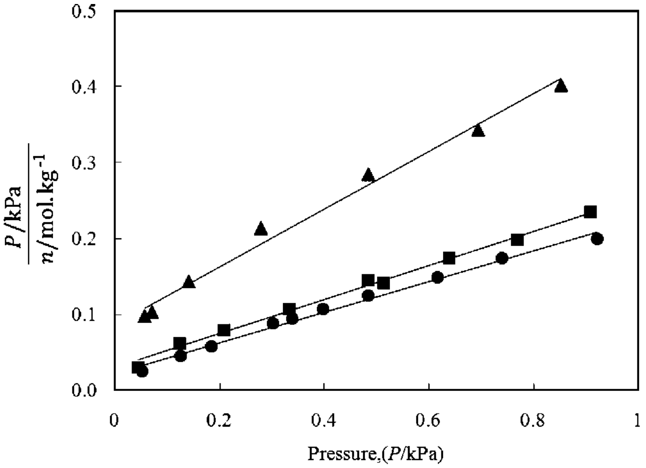

Figure 3. Langmuir domain plot for dichloromethane adsorption on activated carbon: ●, 303.15 K; ■, 318.15 K; ▲, 353.15 K. Solid lines are predictions using best fit parameters of Langmuir model (eq 1). Lines are predictions using the Langmuir model with parameters in Table 3.

Table 3. Parameters of Langmuir Isotherm (Equation 1) for Dichloromethane on Activated Carbon

temperature/K	b/kPa^{-1}	n^{max}/mol·kg^{-1}
303.15	15.38	4.43
318.15	12.47	3.91
353.15	5.90	2.30

4.1. Langmuir Isotherm. The Langmuir isotherm model requires that eq 1 be valid over different temperatures. Such a model would also mean that the saturation loading n_{max} is independent of temperature, a requirement of the original Langmuir derivation. Langmuir behavior is readily observed by plotting P/n against P, which should be a straight line (Figure 3). Although the individual isotherms (at different temperatures) can be well-described by the Langmuir isotherm, the data fitting procedure at each temperature resulted in a different value of n_{max} (Table 3). An attempt to fit data using the Langmuir form in eq 2 yielded poor results. When one fits data for each temperature separately, a total of six adjustable parameters are available (two for each temperature), whereas only three adjustable parameters are available when using eq 2. The effective increase in the number of parameters results in a better fit. Yun and Choi[20] use the Toth isotherm to fit their experimental data.

4.2. Virial Isotherm. Virial domain plots are often helpful to scrutinize the quality of the data.[9] Good quality data often behave smoothly in a virial domain plot, although there is no thermodynamic restriction on the behavior as such. This observation comes from experience. Physical adsorption of most gases and vapors conform to this observation. For the case of dichloromethane on activated carbon, the plots in the virial domain are shown in Figure 4. Moreover, these plots also show a polynomial behavior as evident from eq 3. The virial coefficients at the three experimental temperatures were used to obtain their temperature dependency according to eqs 6 and 7. The fit results are shown in Figure 5, and the parameter values are given in Table 4. The plot for virial parameter k also indicates the variation of Henry's constant with temperature as explained earlier according to eq 5.

A virial isotherm can be used to successfully describe the temperature dependency of the isotherms in this case. However, in general, extrapolation of the virial model to a pressure higher than the experimental conditions used is often unreliable, because of the polynomial nature of eq 6. On the other hand,

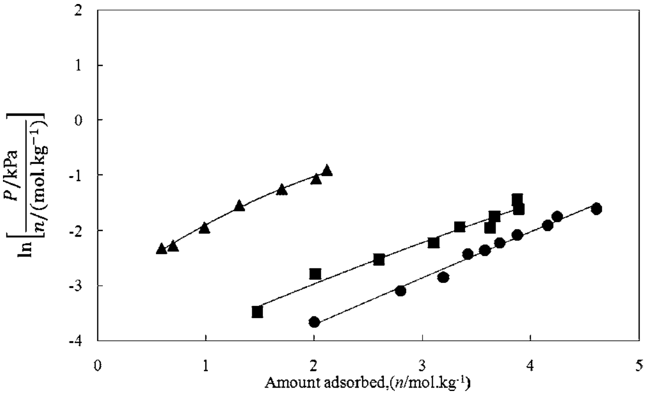

Figure 4. Virial domain plots for dichloromethane adsorption on activated carbon: ●, 303.15 K; ■, 318.15 K; ▲, 353.15 K. Lines are predictions of virial model using parameters in Table 4.

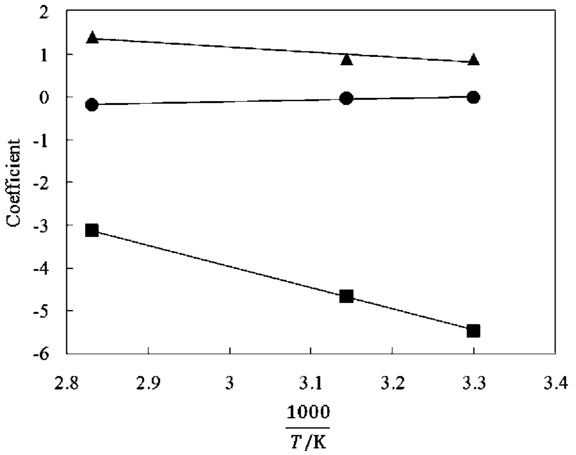

Figure 5. Parameters of eqs 6 and 7. ■, *k*; ▲, *b*; ●, *c*.

Table 4. Parameters for Virial Isotherm Model

k_0	k_1/K	b_0/mol·kg^{-1}	b_1/mol·kg^{-1}·K	c_0/mol^2·kg^{-2}	c_1/mol^2·kg^{-2}·K
10.97	−4976.5	4.77	−1198.7	−1.28	389.27

moderate extrapolation to slightly higher pressures might be safely performed in the case of the Langmuir model (provided the isotherm stays as type I and no capillary condensation occurs).

4.3. Enthalpy of Adsorption. The enthalpy of adsorption, $-\Delta H_{\mathrm{ads}}$, as given by the virial isotherm eq 8 can be readily calculated once the temperature dependency of the virial coefficient is known. It is plotted as a function of loading in Figure 6. Initially it starts with a value of about 41 kJ·mol^{-1} and slightly increases with loading until 1.5 mol·kg^{-1} and falls toward its enthalpy of vaporization (~ 28.6 kJ·mol^{-1}) at high loadings. This closely follows the behavior reported in earlier works[20] and indicates the energetic heterogeneity of the carbon surface. It is interesting to note that Yun and Choi[20] also report a maxima (about 44 kJ·mol^{-1}) in the enthalpy of adsorption at around 2 mol·kg^{-1}, and at around 6 mol·kg^{-1} this value decreases to about 29 kJ·mol^{-1}.

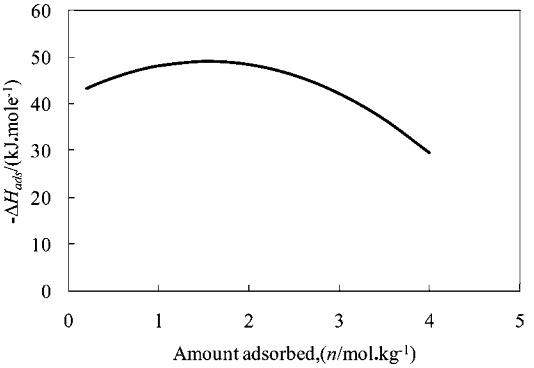

Figure 6. Enthalpy of adsorption calculated from the virial model.

5. Conclusions

In this work we have developed a method for the measurement of adsorption of the VOC dichloromethane on activated carbon using TGA. This method outlines effective usage of TGA, an instrument available in most laboratories, for adsorption measurement of VOC and thereby removes the necessity of a special gravimetric apparatus for these measurements.

Isotherms for three different temperatures, namely, (303.15, 318.15, and 353.15 K), were measured. Although higher partial pressures can readily be obtained, we measured the isotherms up to partial pressures of about 1 kPa; higher partial pressures would be rarely encountered in industry. The isotherms were fit using virial and Langmuir models. It was observed that the best description of experimental data is obtained using a virial isotherm across all of the temperatures. The limiting enthalpy of adsorption obtained using the virial model was −41 kJ·mol^{-1}.

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