Virial Analysis of Methane Adsorption in 5A Zeolite

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In a previous study, Rybolt and Pierotti (1984) analyzed adsorption in microporous carbons using a virial coefficient treatment of adsorption. Second gas-solid virial coefficients, B_{2s}, over a range of temperatures were used in conjunction with a configuration integral that expressed the relation of B_{2s} to the gas-solid interaction potential to extract the energetic and structural parameters necessary to characterize the gas-solid systems. In that study, as a first approximation, the surfaces of the carbon powders were considered to be flat and characterized by surface areas. It was pointed out that virial coefficient treatments of microporous adsorption should include more complicated gas-solid interaction potentials to model three-dimensional pore structures. Everett and Powl (1976) carried out a virial treatment of monatomic gas, Henry's law adsorption in microporous carbons based on a cylindrical pore model. In the present investigation, the methane-5A zeolite system is examined using a modified version of the Lennard-Jones and Devonshire (LJD) cell model of liquids to represent the adsorbate-cavity wall interaction potential. 5A zeolite provides a good model system to study microporous adsorption because the structure is regular and has been well characterized. Methane is selected to determine if this hydrocarbon can be adequately represented as a simple spherical molecule as is done for monatomic gases.

There is considerable interest in zeolitic adsorption because of both industrial applications and theoretical curiosity. In particular there have been a variety of studies based on the methane-5A system as well as other methane-zeolite type A and type X systems. Some of these studies, such as those by Loughlin and Ruthven (1972), Ruthven (1976), and Rolniak and Kobayshi (1980) were directed toward modeling single-component and binary mixture isotherms in 5A zeolite. Cohen de Lara and Kahn (1983) sought to obtain detailed information on the potential energy experienced by methane in type A cavities by using infrared and neutron spectroscopy. Stockmeyer and Monkenbusch (1980) have also studied microscopic molecular motion of methane by using neutron spectroscopy.

Lattice summation calculations based on atom-atom and atom-ion interactions have been used by Bezus et al. (1978) and Kiselev and Du (1981) to calculate thermodynamic values and by Bezus and Kočiřík (1979) to generate detailed interaction potentials within a cavity. Exact lattice summation calculations require the location of all cavity atoms and ions. A modified approach used by Soto (1979) represented the attractive dispersion interaction as a spherical potential based on the LJD cell theory of liquids and treated only the electrostatic induction terms in an exact fashion. This approach was successfully used to generate Henry's law adsorption isotherms.

The basic nature of the approach discussed above is to use atomic interaction and structural parameters to find thermodynamic values. An alternate and reciprocal approach, outlined by Yang (1979) and modified by Rybolt et al. (1987), is to extract molecular energetic and structural parameters from B_{2s}-temperature thermodynamic data. In this work, methane-cavity interactions are based on a spherical potential and compared to prior treatments of monatomic gas-5A zeolite adsorption.

Theory and Analysis

When the Henry's law constant is expressed in (molecules/cavity Pa), then B_{2s} is given by

$$B_{2s} = (K_H \, R \, T \, N_s)/L_0 \tag{1}$$

and in the Henry's law region the moles of gas adsorbed per gram of adsorbent is given by

$$n_{ad} = B_{2s}\,(P/RT) \tag{2}$$

B_{2s} may be represented by a configuration integral (Steele, 1967), which is related to the gas-solid interaction potential by

$$B_{2s} = \int_v [\exp(-u_{1s}/kT) - 1]\,dV \tag{3}$$

To extract from Eq. 3 molecular parameters that characterize a particular gas-solid system it is necessary to have experimental

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B_{2s}-temperature data as well as an appropriate structural model that can be used to represent the gas-solid interaction potential. Stroud (1976) showed that the LJD cell theory of fluids could be modified to model the behavior of an adsorbate molecule inside a zeolite cavity, and Ruthven (1975) showed that methane molecules can retain rotational freedom upon adsorption in a molecular sieve. 5A zeolite has been shown by Seff and Shoemaker (1967) through X-ray crystallographic analysis to consist of a regular array of identical, interconnected, approximately spherical cavities. Eight sodalite units form each cavity and access to each cavity is provided by six windows or openings of mean diameter less than 0.5nm. Since 5A zeolite is a collection of identical cavities, one may consider the total gas-solid interaction as a sum of N_s(cavities/g) individual gas-cavity interactions. By assuming that the cavity potential is spherically symmetrical, and using an integral summation of Lennard-Jones *(6,12) potentials* representing the individual adsorbate-cavity atom interactions, the mean potential within an individual cavity can be determined. In this procedure electrostatic interactions are not explicitly considered but make an implicit contribution to deepening the gas-cavity interaction potential.

The detailed treatment of applying the LJD cell model to this problem is presented elsewhere by Rybolt et al. (1987), but the results may be summarized as follows. The second gas-solid virial coefficient B_{2s} is expressed in terms of four basic parameters: a, N_s, r^*, and E^*. B_{2s} is given as

$$B_{2s} = cg(T, V^*, E^*) \tag{4}$$

where c is a constant given as

$$c = 2\pi a^3 N_s \tag{5}$$

and $g(T, V^*, E^*)$ is an integral function given by

$$g(T, V^*, E^*) = \exp\{-(E^*/T)(V^{*-4} - 2V^{*-2})\} \int_0^1 \exp\{(-E^*/T)[V^{*-4}L(y) - 2V^{*-2}M(y)]\} y^{1/2}\, dy \tag{6}$$

where

$$V^* = (a/r^*)^3 \tag{7}$$

$$y = (r/a)^2 \tag{8}$$

$$L(y) = (1 + 12y + 25.2y^2 + 12y^3 + y^4)(1 - y)^{-10} - 1 \tag{9}$$

$$M(y) = (1 + y)(1 - y)^{-4} - 1 \tag{10}$$

so that the configuration integral is expressed in reduced variables. In this integral representation of the LJD model, the adsorbate molecule is free to move within the fixed spherical cavity of the adsorbent. The potential field felt by the adsorbate depends only on the distance r (y in reduced variables) of the molecule center from the center of the cavity.

Determining the parameter values of a, N_s, and E^* that best fit the experimental virial coefficients is based on the following procedure. A value of V^* is chosen and then a unique selection of E^* is made using Eqs. 4, 5, and 6. Since c is a constant that involves only the structural parameters a and N_s, it should not vary with temperature. Thus the best V^* and E^* pair would be one in which B_{2s}/g is equal to a constant c, a constant that does not vary as the temperature T is changed. In fact, the fit is not perfect and so an average c value is used. The minimum value of the standard deviation of log c is used as the criterion for goodness of fit of selected $V^* - E^*$ values. The standard deviation of log c rather than of c is used so that only the scatter and not the magnitude of the numbers will affect the standard deviation value. As shown in Table 1, methane-5A Henry constants reported by Ruthven (1976) have been converted to the corresponding B_{2s} values using Eq. 1 and the appropriate conversion factors. Note that B_{2s} values can be determined directly from adsorption data, but are less frequently reported than Henry constants although they are conveniently related to gas-solid interaction potentials.

Experimental values of B_{2s} are divided by calculated values of the integral g for a given V^* and E^* pair at each associated temperature. An iterative procedure in which the value of E^* is cycled until the minimum value of the standard deviation of log c is found is used to find the best fit E^* for a range of V^* values. A Macintosh Plus computer using Microsoft Fortran is used for this analysis. The integral in Eq. 6 is evaluated using a numerical integration subroutine QUANC8, which is based on a quadrature adaptive Newton-Cotes eight-panel method presented by Forsythe et al. (1977).

It is not possible to use this same criterion of minimizing the standard deviation of log c to make a unique selection among V^* and E^* pairs. For any V^*, an E^* value can be found that gives a good fit of the data even if the V^* and E^* values are physically unreasonable. In general, as V^* becomes smaller the best fit E^* becomes smaller also. Fortunately, there is another criterion that places a restriction on acceptable V^* and E^* pairs. The interaction energy, $w(r^*)/k$, at equilibrium separation between the adsorbate and cavity wall may be calculated from:

$$\begin{aligned} w(r^*)/k = E^*\{&(1/20)V^{*-11/3}[(1 - V^{*-1/3})^{-10} \\ &- (1 + V^{*-1/3})^{-10}] - (1/4)V^{*-5/3} \\ &\cdot [(1 - V^{*-1/3})^{-4} - (1 + V^{*-1/3})^{-4}]\} \end{aligned} \tag{11}$$

or from (Rybolt et al., 1987):

$$|w(r^*)/k| = [d \ln B_{2s}/d(1/T)] \tag{12}$$

Since Eq. 12 can be used to calculate $w(r^*)/k$ directly from experimental data, this provides a restriction to be placed on allowed pairs of V^* and E^*.

To make an unambiguous selection of V^*, Eq. 11 is used to calculate $w(r^*)/k$ for each V^*-E^* pair. A plot of these $w(r^*)/k$ values vs. V^* generates a curve that goes through a maximum. On each side of the maximum there is one value of V^* that gives

Table 1. Henry's Law Constants and Virial Coefficients for Methane-5A Zeolite

T K	$K_H \times 10^4$ molecules/cavity Pa	$B_{2s} \times 10^{-2}$ cm^3/g
190	25	23
212	6.2	6.5
230	2.5	2.8
253	0.83	1.0
273	0.5	0.7

a $w(r^*)/k$ which agrees with the one calculated from Eq. 12. The higher of these two values of V^* is found to give a slightly better fit of the data and so the higher V^* is selected.

Other fitting procedures could be used to obtain the parameters $\langle c \rangle$, V^*, and E^*. One could combine all the available sets of $B_{2s}(T)$ data for a given adsobent, which in this case could include the Ar, Kr, Xe, and CH_4 adsorbates. From these combined data sets one could use the analysis outlined in this paper and find an average c value that would be the least dependent on both temperature and adsorbate variation. However, this procedure would not give as much information about the individual adsorbate-adsorbent systems and it was considered desirable to see how well the data for each individual adsorbate system fit the model. Another possible approach would be to use Eqs. 11 and 12 to link the value of E^* to V^* and then carry out a best fit procedure as described previously but now requiring a variation of only V^* values until the minimum of the standard deviation of log c was found. This approach might be useful in future work. It was not used here so that the full range of V^*-E^* pairs could be explored and also because it was considered desirable to use an approach for methane that was identical to that used previously for the monatomic gases.

Results and Discussion

Tables 2 and 3 give the results of this analysis for methane and compare them to values obtained for monatomic gases Kr and Xe from Rybolt et al. (1987) and Ar from Rybolt (1987) where the use of a simple spherical molecular potential is exact. It is important to note that the argon analysis from Rybolt (1987) has been revised relative to Rybolt et al. (1987). This change is due to the availability of additional B_{2s} data, which changes the best fit parameters for the Ar-5A system and illustrates how sensitive this fitting procedure is to the quality of the B_{2s} data.

The procedure described previously was used to find $w(r^*)/k$, V^*, and E^* that gave the most consistent prediction of the available experimental data based on the theoretical equations and judged by determining the minimum value of the standard deviation of log c. Also found from this analysis was the average value of the constant c. Equations 5 and 7 were used in conjunction with an estimate of r^* to find values of a and N_s. Soto (1979) used the distance of closest approach between a methane molecule and zeolite solid based on an oxygen-oxygen surface diameter of 0.276 nm and a methane gas diameter of 0.367 nm. By assuming that the radii are additive, a methane-zeolite hard-sphere separation of 0.322 nm was found. The corresponding equilibrium separation was based on a Lennard-Jones (6, 12) potential (Pierotti and Thomas, 1971) and was found to be 0.361 nm.

Equation 12 was used in conjunction with the B_{2s} data to find the $w(r^*)/k$ values shown in Table 2. The best E^* and V^* values were found by using the fitting procedures outlined in the previous section, which gives V^* and E^* pairs leading to the minimum of the standard deviation of log c and also gives a $w(r^*)/k$ value from Eq. 11 that agrees with the value calculated from the slope of ln B_{2s} vs. $1/T$. The values of a determined from this analysis (for methane a = 0.715 nm) agree well with the X-ray crystallographic average of 0.709 nm (radial distances vary from 0.704 to 0.723) for the oxygen atoms that form the interior of 5A zeolite.

Table 2. Energetic and Fitting Parameters

Gas	$w(r^*)/k$ K	E^* K	V^*	Std. Dev. of log c
Argon	1,381	14,459	8.12	0.03371
Krypton	1,859	18,404	7.90	0.07447
Methane	2,247	21,510	7.76	0.04484
Xenon	2,694	25,555	7.72	0.14040

Table 3. Structural Parameters

Gas	$\langle c \rangle$ cm³/g	r^* nm	a nm	$N_s \times 10^{-20}$ cavities/g
Argon	0.294	0.343	0.689	1.43
Krypton	0.304	0.355	0.708	1.37
Methane	0.230	0.361	0.715	1.00
Xenon	0.154	0.374	0.739	0.61

The other structural parameter, N_s, varies from one gas to another but decreases with increasing molecular size and is lower than the known value of 3.59×10^{20} (cavities/g) based on X-ray crystallographic studies. However, the structural model used does not make any attempt to account for the interior cavity wall surface that is missing due to the presence of the cavity windows. This lost surface area is approximately 50% in 5A zeolite, and if this factor were included in Eq. 7 when N_s is calculated from $\langle c \rangle$ then the calculated N_s values would roughly double. Thus the exclusion of cavity windows in the LJD model is responsible for much of the apparent discrepancy between calculated and actual values of N_s for 5A zeolite. In addition, the value of $\langle c \rangle$ and hence N_s is very sensitive to changes in the B_{2s}-temperature values, so that having good B_{2s} values is essential to an exact analysis. For example, the Xe-5A data have the poorest fit and also the lowest N_s value. It may also be that a more exact potential that includes the effect of the windows would be more significant for larger adsorbate molecules and hence adjust the drop in methane and xenon N_s values more than Ar and Kr. Considering the approximations inherent in this analysis, it is perhaps surprising that this analysis, which only takes only equilibrium separation as an *a priori* parameter, works as well as it does.

Note that the methane adsorbate seems to be handled as well as the monatomic gas adsorbates by use of a uniform spherical potential. Also note that the trend in $w(r^*)/k$ and E^* is what one would expect as the adsorbate size increases; methane fits into this trend and supports the use of a virial coefficient treatment for microporous solids. A virial approach is particularly useful where the adsorbent structure, as for example in a microporous carbon, can not be well characterized, thus making an exact lattice sum calculation impossible.

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Notation

a = cavity radius
B_{2s} = second gas-solid virial coefficient
c = structural constant
$\langle c \rangle$ = average of c
E^* = gas-cavity interaction energy, K; $E^* = \epsilon_{1s}/k$
g = Lennard-Jones and Devonshire cell model integral

k = Boltzmann constant
K_H = Henry's law constant
L = first polynomial in y
L_o = Avogadro's number
M = second polynomial in y
n_{ad} = moles gas adsorbed per gram adsorbent
N_s = number of sites or cavities per gram adsorbent
P = pressure of adsorbate
r = radial distance of adsorbate from center of cavity
r^* = equilibrium separation between center of adsorbate molecule and center of cavity wall atom
R = universal gas constant
T = temperature, K
u_{1s} = gas-solid interaction potential
V^* = reduced cavity volume
w = gas-wall mean interaction potential energy
y = reduced radial position of adsorbate relative to center of cavity
ϵ_{1s} = maximum gas-cavity interaction energy, J

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