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Full Length Article

A re-assessment of the isosteric heat for CCl_4 adsorption on graphite

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ABSTRACT

We have carried out molecular simulations of carbon tetrachloride adsorption on graphite, in order to investigate the role of the octopole in potential models for the CCl_4/graphite system, and the temperature dependence of the first-order gas-liquid transition in the first adsorbate layer. Two classes of potential model for carbon tetrachloride were considered: the first has 5 *LJ* sites and the second includes five partial charges to model the leading octopole. Both models are adequate to represent the vapour-liquid equilibrium, suggesting that the octopole makes an insignificant contribution to the properties of the bulk phase. Both models show that adsorbed CCl_4 molecules are delocalized on a graphite surface because of the strong intermolecular interactions. It is found that the *LJ* sites on the chlorine atoms, not the octopole, play the most important role in matching the experimental isotherm and isosteric heat data with simulation. The heat is constant, across the first-order transition of the first adsorbate layer. The simulation results show that both the magnitude of the density jump, and the isosteric heat across the first-order transition, decrease as the temperature increases. This is in qualitative agreement with the 1972 experimental data of Avgul and Kiselev, but these experimental data exhibit an unusually strong decrease in the isosteric heat, and the coexistence region between the two phases displays an unusual asymmetrical shape. Detailed analysis of our simulation results, together with the calculated isosteric heat from the experimental isotherms of Machin and Ross, show that there may be errors associated with the heat data of Avgul and Kiselev at high temperatures.

1. Introduction

Carbon tetrachloride (CCl_4) is widely used in industry as a solvent. Since it is harmful to health and to the environment, it is desirable to capture the vapour. A preferred method is by removal by carbonaceous adsorbents because of their low cost relative to other adsorbent materials. The toxicity of carbon tetrachloride incurs a high cost in safety requirements for laboratory experiments; this can be minimized by resort to computer simulation. As a fundamental study, the system attracts interest because of the role played by the tetrahedral structure of the molecule on the microscopic structure of the adsorbate, since the density of the first adsorbate layer is sensitive to molecular orientation. Possibly for the reason mentioned above, experimental studies on adsorption of carbon tetrachloride are limited. Isotherms in the temperature range between 225 K and 293 K[1] were reported by Pierce [1], and Machin & Ross [2]. The accuracy of these isotherm data was discussed in Do and Do [3]. Isosteric heat data covering the same temperature range were reported by Avgul and Kiselev [4,5]. For the heat curves in the sub-monolayer coverage region at temperatures less than 250 K the heat is constant across the gas-liquid first-order transition, in agreement with X-ray data [6]. The constant heat during the 2D-condensation is due to the growth of 2D-adsorbate patches, separated from rarefied regions in the first adsorbate layer [7,8]. As the temperature increases the heat data of Avgul and Kiselev shows that, the region of constant heat shrinks, but that the heat decreases too quickly and the two-phase coexistence region does not have the symmetrical shape exhibited by other adsorbates [9–12]. Although they did not report data for adsorbed density versus pressure, the isotherms reported by Machin and Ross over the same temperature range have been used in the present paper to assess the heat data from the Clausius-Clapeyron equation.

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[1] The bulk triple and critical temperatures are 249K and 556K.

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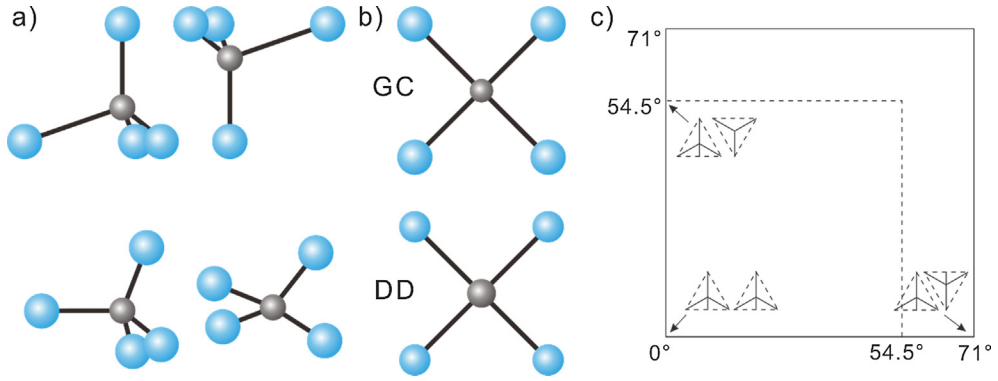

Fig. 1. Illustration of the favoured pairwise configurations of tetrahedral molecules; (a) face-to-face and face-to-edge configurations, (b) the geometrical structure of the molecular *GC* [24] and *DD* [3] models, and (c) possible configurations of the assembly of 2 molecules on a surface.

2. Simulation details

2.1. Fluid and solid model

The *X*-ray and neutron diffraction data on the intra- and inter-molecular structure [13–16] give a C—Cl bond length of between 1.77 Å and 1.85 Å, and the closest inter-molecular (C—C) distance is between 6.2 Å and 6.7 Å. These values are used in the development of potential models for carbon tetrachloride. Early potential models which treat CCl_4 as a 1-site molecule [16–19], fail to describe the thermodynamic properties of CCl_4 because the interaction between chlorine atoms is much stronger than that between the carbon atoms, which means that the positions of the four chlorine atoms is important. A more accurate model, must therefore, account for all atoms in the tetrahedral CCl_4 molecule. Previously, 5-site models have been shown to give a good account of the vapour-liquid equilibrium (*VLE*) as well as adsorption of CCl_4 on graphite [20–23]. These potential models have been reviewed in Do and Do [3]. Recently a new model in this class was proposed by Guevara-Carrion et al. which includes partial charges to model the leading electrostatic octopole [24]. In bulk liquid or solid CCl_4, most models show that a face-to-face interlocking structure is the most favoured configuration as shown in Fig. 1a [10,22]. On graphite, Avgul and Kiselev [11,12] discussed three typical configurations: (1) a tripod configuration with three chlorine atoms facing the surface, (2) an edge-down configuration with two Cl atoms facing the surface, and (3) an inverted tripod configuration. The monolayer density depends on the orientation of the molecules; for example, a first adsorbate layer comprised of only the energetically favourable tripod configuration gives the lowest monolayer density. Combination of the configurations detailed above at finite temperatures is possible because of the balance between the energy and the entropy to minimize the free energy [25].

In this simulation study, we have focussed on two potential models: (1) the 5-site (*LJ*) model proposed by Do and Do (*DD*) [3], (2) the 10-site (5*LJ* + 5*q*) model of Guevara-Carrion et al. (*GC*) [30]. The molecular parameters for these models are listed in Table 1.

It is to be noted that although the *GC* model has a larger separation between the dispersive site on the carbon atom and the other dispersive sites, the overall molecular size conforms to the experimental data because collision diameters used are smaller than those of the *DD* model (Fig. 1b).

Depending on the size and shape of the adsorbate molecules, the first adsorbate layer may form a packing that is commensurate with the graphite lattice; for symmetrical tetrahedral adsorbates, the possible lattice for an adsorbate in a hexagonal centred packing (HCP) are $\sqrt{3}a_{Gr}$, $2a_{Gr}$, $\sqrt{7}a_{Gr}$, $3a_{Gr}$, *etc.*, where $a_{Gr} = 0.246nm$ is the graphite lattice constant. For instance, methane forms a $\sqrt{3} \times \sqrt{3}a_{Gr}$ packing [26–28], CF_4 forms a $2 \times 2a_{Gr}$ packing [29,30], and CCl_4 with a size between $\sqrt{7}a_{Gr}$ and $3a_{Gr}$, the monolayer density is 3.96 μmol/m^2 if it adopts a $\sqrt{7}a_{Gr}$ commensurate packing (Table 2).

We used two models for graphite. The first model treats graphite as a continuum solid with an energetically homogeneous surface; the potential energy of interaction with an *LJ* site is given by the 10–4–3 equation (Eq. (1)) with the molecular parameters derived by Steele [31].

$$\varphi_{sf} = 2\pi(\rho\sigma_{sf}^2)\varepsilon_{sf}\left[\frac{2}{5}\left(\frac{\sigma_{sf}}{z}\right)^{10} - \left(\frac{\sigma_{sf}}{z}\right)^{4} - \frac{1}{3}\frac{\sigma_{sf}^4}{\Delta(z+0.61\Delta)^3}\right] \quad (1)$$

The second is the Corrugation and Anisotropy (CA) model that accounts for the hexagonal arrangement of carbon atoms and the anisotropy of polarizability of graphite [32]. Details of this model are given in Refs. [33,34]

2.2. Simulation details

Simulations were carried out using the kinetic Monte Carlo (*k*MC) method in the canonical and grand canonical ensembles [35–37]. *k*MC provides a very efficient method for the calculation of chemical potential. Instead of using the ensemble average, as in Metropolis Monte Carlo, the *k*MC scheme assigns a time of existence for each configuration, defined as the inverse of the sum of molecular mobilities, *R*:

$$\tau = \frac{\ln(1/\xi)}{R} = \frac{\ln(1/\xi)}{\sum_j \exp(u_j/k_B T)} \quad (2)$$

where ξ is a random number, introduced to maintain a stochastic sampling in the *kMC* simulation, and u_j is the potential energy of interaction molecule "*j*" with all entities in the system. The isosteric heat in the grand canonical simulations was obtained from number and

Table 1
Molecular parameters for the various CCl_4 potential models.

Model	Atom	Collision diameter (nm)	Reduce well depth (K)	Bond length (nm)	Charge	Reference
DD	C	0.46	39	0.1766	–	[3]
	Cl	0.35	105			
GC	C	0.281	12.37	0.2044	−0.362	[24]
	Cl	0.325	212.6		0.0905	

Table 2
Lattice constants and the adsorbate commensurate density.

Packing	Lattice constant (nm)	Surface density (μmol/m^2)
$\sqrt{3}a_{Gr}$	0.426	10.54
$2a_{Gr}$	0.492	7.92
$\sqrt{7}a_{Gr}$	0.651	3.96