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Adsorption Compression Analysis for Supercritical Fluids using Ono-Kondo Model

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In this paper, supercritical data has been evaluated and shown to demonstrate adsorption compression. Ono-Kondo analysis of adsorption isotherms for supercritical systems (including nitrogen, methane, and carbon dioxide on activated carbon Filtrasorb 400 and on zeolite 13X) indicates adsorption compression phenomenon at high pressure end just as in subcritical systems. Experimental isotherms for adsorption of supercritical fluids are plotted in Ono-Kondo coordinates with the Henry's constant estimated based on results of modeling as well as calorimetric and chromatographic measurements. The linear sections of the results show the range of applicability of the classical Ono-Kondo model with constant energies of interactions. The slopes of these linear sections represent values and signs of these energies: negative slopes indicate repulsive interactions in adsorbed phase due to adsorption compression. Switching interactions from attractive to repulsive with an increase in the pressure for supercritical adsorption suggests that adsorbed phase has two regions. One is an attractive region at low-pressures and the other is a repulsive region at high pressures. It can be indicated that the shape of isotherms in Ono-Kondo coordinates can help to understand adsorbate-adsorbate energies; the slope of the line in Ono-Kondo coordinates gives the sign and magnitude of the energy as a function of adsorbate density.

Keyword: Adsorption Compression, Ono-Kondo model, Supercritical Fluids

INTRODUCTION

This work is based on ideas originally proposed by Ono and Kondo [1] for density gradients at fluid-solid interfaces. The Ono-Kondo model is able to predict a wide variety of behavior including multilayer adsorption [2], hysteresis in micropores [3], and adsorption in supercritical systems [4]. It also has been discussed for a phenomenon of compression in adsorbed phases at subcritical conditions [5]. In compressed systems, molecules adsorb to highly attractive surface to reach densities greater than in a normal liquid. Strong attractions to the surface can cause more molecules to pack in the fast layer than in a normal liquid and therefore create highly repulsive interactions among nearest neighbors. Thus compression is introduced by having repulsive nearest neighbor interactions [6]. This phenomenon has various demonstrations, including compression of molecules sitting on neighboring active sites of a solid surface, compression of adsorbed surface layers, and compression in nanopores [7-9]. In this paper, we consider a new aspect of compression behavior for supercritical adsorption by using Ono-Kondo lattice model.

MODELING ANALYSIS

To derive the adsorption isotherm, this applies concepts first proposed for lattice systems by Ono and Kondo [1] and using the equation developed by Aranovich and Donohue as a guideline [8]. Consider taking an adsorbate molecule from the surface and moving it to an empty volume between molecules in the bulk (far from the surface). This is equivalent to the exchange of the molecule with a vacancy that it fills

$$M_S + V_b = V_S + M_b \qquad (1)$$

Where M_s is the adsorbate molecule on the surface, M_b is the adsorbate molecule in the bulk, V_s is the vacancy on the surface, and V_b is the vacancy in the bulk.

If this exchange occurs at equilibrium, then;

$$\Delta U - T\Delta S = 0 \qquad (2)$$

Where ΔU and ΔS are the internal energy and entropy changes and T is the absolute temperature. The value of ΔS can be represented in the form;

$$\Delta S = k \ln \frac{(a/a_m)(1-x_b)}{(1-a/a_m)x_b} \qquad (3)$$

Where k is Boltzmann's constant, x_b is the density of adsorbate in the bulk, a is the density (number of adsorbed molecules per square meter) and a_m is the maximum density of adsorbate molecules that can be on the surface.

The change in internal energy is:

$$\Delta U = \varphi_s + U_f - U_g \qquad (4)$$

Where φ_s is an average energy of the molecule-surface interaction, U_f is the energy of interaction between a central molecule and surrounding molecules in the 2-D fluid, and U_g is the energy of interaction between a central molecule and surrounding molecules in the 3-D gas.

Substituting equations (3) and (4) into equation (2)

$$k \ln \frac{(a/a_m)(1-x_b)}{(1-a/a_m)x_b} + \varphi_s + U_f + U_g = 0 \qquad (5)$$

For soft molecules (real molecules and Lennard-Jones molecules), can be defined the energy of interaction between a central molecule and surrounding molecules in the 2-D fluid as:

$$k \ln \frac{(a/a_m)(1-x_b)}{(1-a/a_m)x_b} + \varphi_s + U_f + U_g = 0 \qquad (6)$$

Where λ is a coefficient (<1) which accounts for the fact that each neighbor can belong to several clusters, $\lambda = 2\pi r^{*2} g_0$, g_0 is the positive coefficient not depending on distance (in the mean-field, adsorbed phase critical point occurs at $2\pi g_0 = 6$), a is the density in the 2-D fluid (number of adsorbed molecules per square meter), $\varphi(r^*)$ is potential function at a distance, r^* which consider from two cases as:

$$r^* = \begin{cases} 2^{1/6}\sigma & \text{for low densities} \\ r_0(a) & \text{for high densities} \end{cases} \tag{7}$$

r_0 is the average distance between molecules in the dense monolayer. And can be written the energy of interaction between a central molecule and surrounding molecules in the 3-D gas in a similar form

$$U_g = \lambda^{/} x_b \varphi\left(r^{*/}\right) \tag{8}$$

Where $\lambda^{/}$ and $r^{*/}$ are 3-D analogs of λ and r^* for gas phase. And plugging equations (6) and (8) into equation (5)

$$\ln\frac{(a/a_m)(1-x_b)}{(1-a/a_m)x_b} + \frac{\varphi_s}{kT} + \frac{\lambda a\varphi(r^*)}{kT} - \frac{\lambda^{/} x_b \varphi(r^{*/})}{kT} = 0 \tag{9}$$

In the equation (9), the first two terms dominate and can be combined to:

$$Y = \ln\frac{(a/a_m)(1-x_b)}{H(1-a/a_m)x_b} \tag{10}$$

Where the Henry's constant is,

$$H = \exp\left(\frac{-\varphi_s}{kT}\right) \tag{11}$$

Therefore, equation (9) can be represented in the following form:

$$\frac{Y}{x_b} = -\frac{\lambda\varphi(r^*)}{kT}\frac{a}{x_b} + \frac{\lambda^{/}\varphi(r^{*/})}{kT} \tag{12}$$

When plotted Y/x_b versus a/x_b can get the value of $\lambda\varphi(r^*)$ from the slope of the graph. The sign of $\lambda\varphi(r^*)$ gives information about the sign of adsorbate-adsorbate interactions. Moreover, plotting Y/x_b as a function of a/x_b also give the intercept, $\lambda^{/}\varphi(r^{*/})$, which can be used to verify the assumption that the term of energy of interaction between a central molecule and surrounding molecules in the 3-D gas.

RESULTS AND DISCUSSIONS

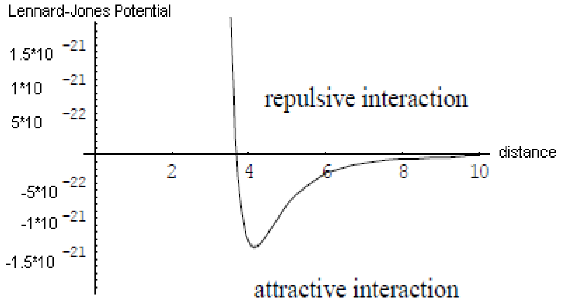

Fig. 1 : Lennard–Jones potential function of fluid

To understand the interactions between adsorbate - adsorbate and adsorbate - adsorbent can be considered the adsorbed molecules take place in two stages for certain specific interactions. The energy of interactions between adsorbate molecules can be described by the Lennard–Jones potential function as shown in Figure 1. These interactions can be occurred between adsorbed molecule and surface of adsorbent, or can be occurred between adsorbed molecule and other adsorbed molecules. One of interactions is an attractive (positive slope) and another one is repulsive (negative slope) interaction.

Table 1: Dimensionless Henry's constants for adsorption of nitrogen, methane, and carbon dioxide on different adsorbents

Adsorbate	H	$-\frac{\varphi_s}{RT}$
on activated carbon Filtrasorb 400 at 318.2 K		
N_2	45	3.8
CH_4	60	4.1
CO_2	100	4.6
on zeolite 13X at 308 K		
N_2	80	4.4
CH_4	120	4.8
CO_2	3000	8.0

To analyze the transition to adsorption compression, we plot isotherms in coordinates of equation (12) with estimated values of H in Table 1. In principle, the value of H can be estimated from the slope of the isotherm at the small pressures. However, we present estimates for normalized H which are in a reasonable ranges in terms of results known from statistical modeling and from chromatographic and adsorption measurements [10-12]. Tables 1 also gives values of $-\frac{\varphi}{RT}$ calculated from H by using equation (11).

When plotted Y/x_b versus a/x_b following form of equation (12), the slope of this line gives the value of $\lambda\varphi(r^*)$ and the sign of $\lambda\varphi(r^*)$ gives information about the character of adsorbate-adsorbate interactions – whether they are attractive or repulsive.

Note that in low-pressure gas $x_b <<< 1$ and the value of Y in equation (12) can be simplified to:

$$Y = \ln\frac{(a/a_m)}{H(1-a/a_m)x_b} \qquad (13)$$

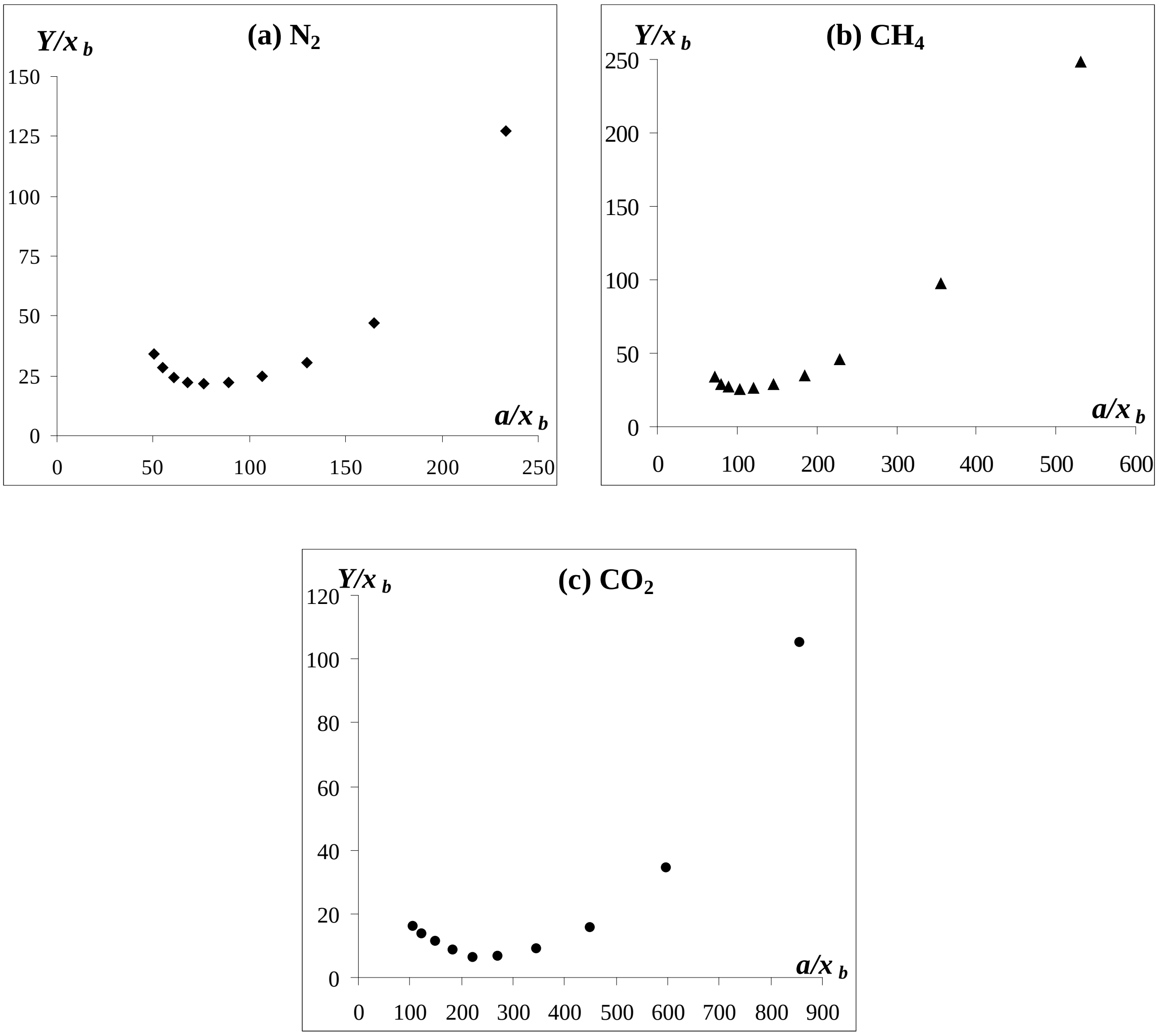

Fig.2 : Adsorption isotherms for (a) nitrogen, (b) methane and (c) carbon dioxide on activated carbon Filtrasorb 400 at 318.2 K (calculated by using experimental data from ref. [13]) in Ono-Kondo coordinates with estimated H given in Table 1

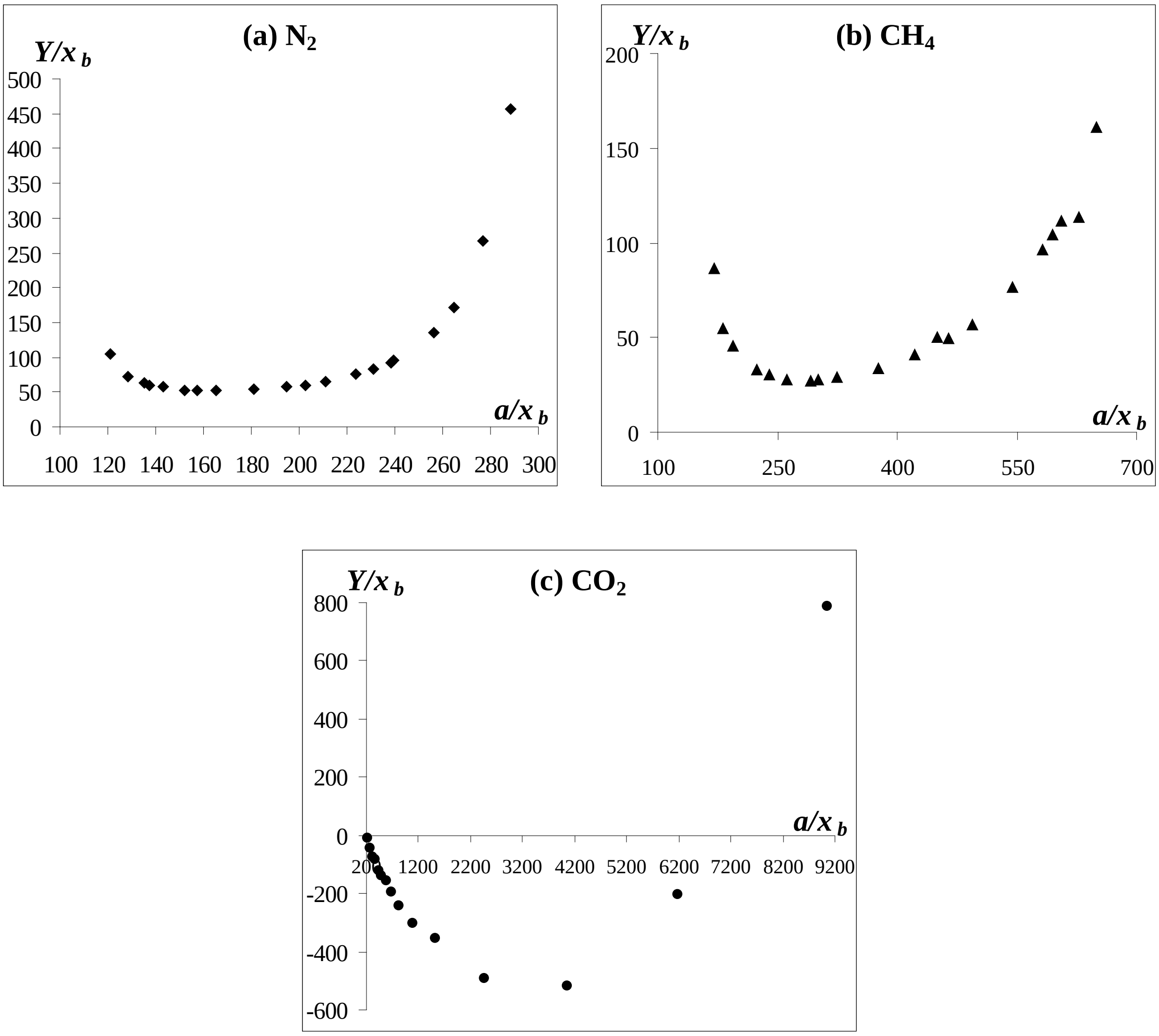

Fig.3 : Adsorption isotherms for (a) nitrogen, (b) methane and (c) carbon dioxide on zeolite 13X at 308 K (calculated by using experimental data from ref. [14]) in Ono-Kondo coordinates with estimated *H* given in Table 1

Figures 2 and 3 show adsorption isotherms in Ono-Kondo coordinate with estimated *H* for N_2, CH_4, and CO_2 on activated carbon Filtrasorb 400 and on zeolite 13X (calculated by using experimental data from ref. [13] and [14], respectively). These isotherms have similar shapes: going down to a minimum and then going up. This shape is consistent with interpretation of the derivative of this function representing potential function for adsorbate-adsorbate interactions. The reason for such a behavior is adsorption compression arising from competition between attraction of the adsorbate to the adsorbent surface and repulsions between/among neighboring adsorbate molecules [6, 9].

Figures 4 and 5 show adsorption isotherms for nitrogen, methane, and carbon dioxide in Ono-Kondo coordinates at high pressure end, comparison of these figures indicates that adsorption compression of nitrogen, methane, and carbon dioxide in pores of zeolite is much stronger than in pores on Filtrasorb 400. This is to be expected.

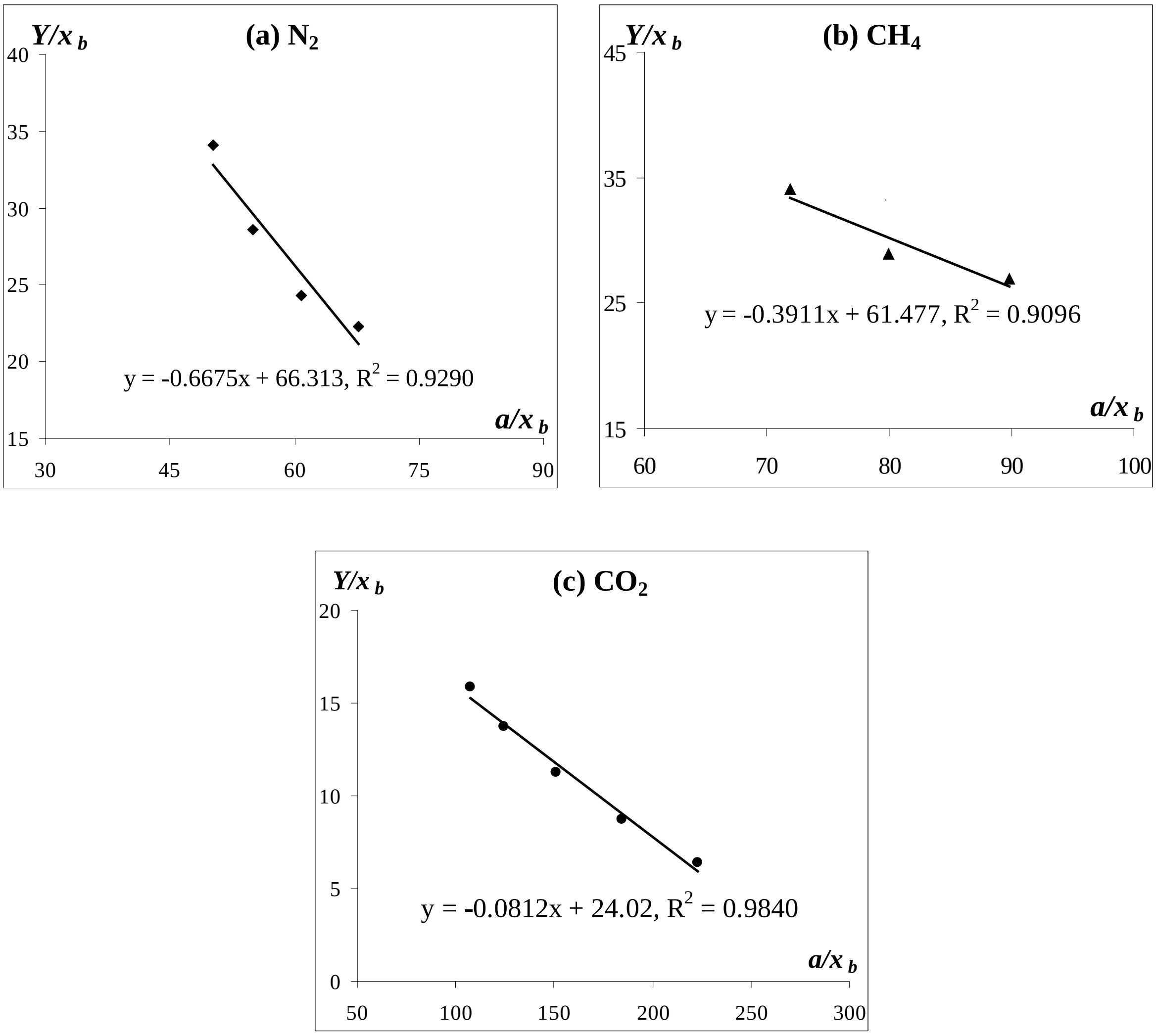

Fig 4 : Adsorption isotherms for (a) nitrogen, (b) methane and (c) carbon dioxide on activated carbon Filtrasorb 400 at 318.2 K which shows high pressure ends in larger scale

Note that at low pressure, neighbors in adsorbate attract each other. As pressure goes up, the distance between adsorbate molecules can become less than in a normal liquid and nearest neighbors repel each other. This is possible because the decrease of free energy due to attraction to the adsorbent is greater than the increase of free energy due to repulsions between adsorbate molecules. At the point where the adsorbate-adsorbate interactions go from attractive to repulsive, the average adsorbate-adsorbate energy is zero and this point corresponds to minimum in isotherms shown in Figures 4 and 5.

CONCLUSIONS

With estimated values of *H*, adsorption isotherms in Ono-Kondo coordinates show deviations from behavior of compression phenomenon at high pressure end. The slopes of these linear sections represent values and signs of these energies: negative slopes indicate repulsive interactions in adsorbed phase due to adsorption compression.

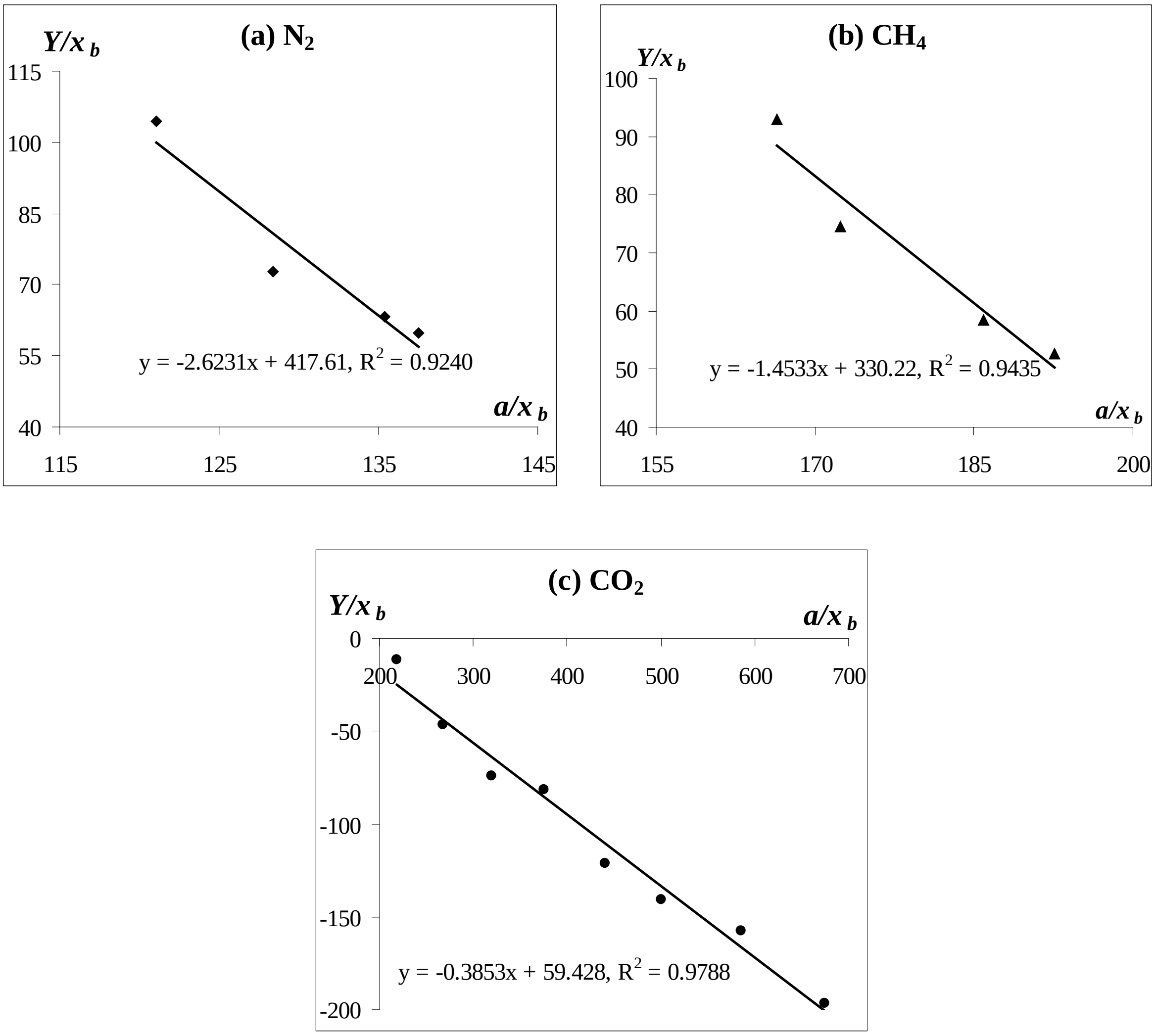

Fig 5: Adsorption isotherms for (a) nitrogen, (b) methane and (c) carbon dioxide on zeolite 13X at 308 K which shows high pressure ends in larger scale

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