Analysis of adsorption compression for CH_4/CO_2 mixture in supercritical systems

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ABSTRACT

The Ono-Kondo model is used to correlate with experimental data from references for the adsorption of methane and carbon dioxide binary mixture on activated carbon Filtrasorb 400 at 318 K and on Norit R1 Extra at 298 K. CH_4-CH_4 interaction in adsorbed layer can be analyzed by using coordinates of equation (4) while CO_2-CO_2 interaction can be evaluated by using coordinates of equation (5). The energy of adsorbate-adsorbate interactions (between a central molecule and surrounding molecules in the adsorbed phase) varies from positive at low pressures to negative at high pressure ends. This result indicates phenomenon of adsorption compression with repulsive interactions in adsorbed phase. The shape of isotherms in Ono-Kondo coordinates can be interpreted in terms of adsorbate-adsorbate interactions: the slope versus density represents potential function where the distance between nearest neighbors is a function of adsorbate density. This transition indicates the competitive nature of the individual component adsorption from the mixtures. CO_2 is most adsorbed component. Even if the concentration of CO_2 in the bulk is lowered, the adsorption competitive stays in favor of CO_2.

Keyword: Supercritical binary mixtures, Adsorbate-adsorbate interactions, Adsorption Compression, Ono-Kondo model.

INTRODUCTION

Nowadays, it is well known that the global warming is a serious worldwide problem. Carbon dioxide emission represents the main cause. One of the ways to reduce this greenhouse gas emission is to capture carbon dioxide in their sources and then store them in the earth. The capture of carbon dioxide in the storage locations has been used adsorption technology. It can be

enhanced by injecting carbon dioxide at supercritical conditions into coal-bed methane reservoirs [1-4]. The carbon dioxide displaces methane from the coal seam and is itself permanently stored. Finally, recovery methane can be useful and carbon dioxide can be converted to fossil fuel in suitable sources.

In order to predict the competitive adsorption behavior of carbon dioxide and methane mixture under supercritical conditions, we must understand in their interaction properties. Because an adsorption of carbon dioxide and desorption of methane have shown the effects for the quantity and quality of the carbon dioxide sequestering and the methane recovering in the enhance coal-bed methane process [5]. Therefore, the knowledge of the adsorption behavior of the mixture of carbon dioxide and methane requires for investigating.

Previously, a lattice DFT model based on the Ono-Kondo equation can be successfully applied to the adsorption of binary systems [6]. This model is able to predict a wide variety of behavior including multilayer adsorption [7], hysteresis in micropores [8], and adsorption in supercritical systems [9]. It also has been discussed for a phenomenon of compression in adsorbed phases at subcritical conditions [10]. The compression 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 [11-14]. In other words, The Ono and Kondo lattice model has been used to predict adsorption isotherms over wide temperature and pressure ranges [15].

In this paper, we consider a new aspect of model to analyze an important fluid-fluid interaction property for methane and carbon dioxide binary mixture in supercritical systems by using Ono-Kondo lattice model. 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 value of coefficient and the sign of coefficient gives information about the character of adsorbate-adsorbate interactions for both components of binary mixtures.

MODELING

Consider a binary lattice with boundaries. Each site of the lattice can contain either an *A* molecule or a *B* molecule or it can be vacant. There are interactions between nearest neighbors with $\varepsilon_{AA}, \varepsilon_{BB}, \varepsilon_{AB}$ being the energy of adsorbate-adsorbate interactions, and $\varepsilon_{AS}, \varepsilon_{BS}$ being the energy of adsorbate-adsorbent interactions. It can be assumed that the lattice fluid is in contact with a flat surface at the plane of *i=0* and that the first layer of adsorbed molecules is in the plane of *i=1*. Figure 1 illustrates the lattice model for both the adsorbate-adsorbate and adsorbate-adsorbent interactions in the monolayer adsorption.
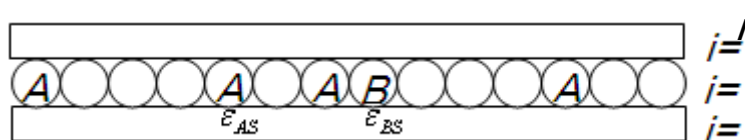

Figure 1 Schematic representation of the lattice model in the first layer for binary system.

In the model exhibited in Figure 1, *i=0* represents the surface plane, *i=1* defines the first layer of adsorbate molecules, *i=2* defines the second layer, and so on. The last layer, *i=N+1*, defines the bulk fluid. According to the Ono-Kondo lattice model [16] can be represented as nonlinear finite difference equations of second order which relate the composition in each layer to the density in

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the bulk for *A* molecule as:

$$kT \ln \frac{x_A(1 - x_{A\infty} - x_{B\infty})}{(1 - x_A - x_B)x_{A\infty}} + \frac{(z_3 - z_2)}{2} \varepsilon_{As} + z_2 x_A \varepsilon_{AA} + z_2 x_B \varepsilon_{AB} +$$

$$\frac{(z_3 - z_2)}{2} x_{A\infty} \varepsilon_{AA} + \frac{(z_3 - z_2)}{2} x_{B\infty} \varepsilon_{AB} - [z_3 x_{A\infty} \varepsilon_{AA} + z_3 x_{B\infty} \varepsilon_{AB}] = 0 \tag{1}$$

Where k_B is Boltzmann's constant, T is absolute temperature, z_1 is the coordination number between the surface and molecules in the first layer, z_2 is the coordination number in the monolayer, and z_3 is the coordination number for tree-dimensional lattice. Here, x_∞ denotes the bulk concentration (or density), x_i is the concentration (or density) in the *i-th* adsorbed layer, ε represents the nearest-neighbor energy of the adsorbate-adsorbate interactions, and ε_s is the interaction energy between the adsorbate molecules on the adsorbent surface. Both ε and ε_s are negative for the attractive forces. Notice that the equations for *i=1* and *i=N* define the boundary conditions on the lattice model.

Rearrangement equation (1) becomes to:

$$kT \ln \frac{x_A(1 - x_{A\infty} - x_{B\infty})}{(1 - x_A - x_B)x_{A\infty}} + \frac{(z_3 - z_2)}{2} \varepsilon_{As} + z_2(x_A \varepsilon_{AA} + x_B \varepsilon_{AB}) -$$

$$\left(\frac{z_3 + z_2}{2}\right)(x_{A\infty} \varepsilon_{AA} + x_{B\infty} \varepsilon_{AB}) = 0 \tag{2}$$

Similarly, for B molecule:

$$kT \ln \frac{x_B(1 - x_{A\infty} - x_{B\infty})}{(1 - x_A - x_B)x_{B\infty}} + \frac{(z_3 - z_2)}{2} \varepsilon_{Bs} + z_2(x_A \varepsilon_{AB} + x_B \varepsilon_{BB}) -$$

$$\left(\frac{z_3 + z_2}{2}\right)(x_{A\infty} \varepsilon_{AB} + x_{B\infty} \varepsilon_{BB}) = 0 \tag{3}$$

For the mean field approximation, we can write equation (2) as:

$$\frac{1}{x_B} \ln \frac{x_A}{(1 - x_A - x_B)x_{A\infty}H_A} = -\frac{z_2 \varepsilon_{AA}}{kT}\frac{x_A}{x_B} - \frac{z_2 \varepsilon_{AB}}{kT} \tag{4}$$

And equation (3) becomes to:

$$\frac{1}{x_A} \ln \frac{x_B}{(1 - x_A - x_B)x_{B\infty}H_B} = -\frac{z_2 \varepsilon_{BB}}{kT}\frac{x_B}{x_A} - \frac{z_2 \varepsilon_{AB}}{kT} \tag{5}$$

Where $H_A = (\exp(z_2 - z_3)/2)\varepsilon_{AS}/kT$, $H_B = (\exp(z_2 - z_3)/2)\varepsilon_{BS}/kT$, and the values of $x_{A\infty}$ and $x_{B\infty}$ can be approximated by $x_{A\infty} = (\pi/6)n\sigma^3_A$, here n is the total number of particles per volume of the container, and σ is the distance between molecules. Note that n is calculated from the classical ideal gas law as $n = n_m N_A / V = P / kT$, where P is pressure of the fluid [Pa], V is total volume of the container containing the fluid [m³], n_m is the number of moles [mole], N_A is Avogadro number [molecules/mole], k is Boltzmann's constant [J/K], and T is absolute

temperature [K].

Plotting $[\quad 1/x_B \ln x_A /(1-x_A-x_B)x_{A\infty}H_A \quad]$ versus $[\quad x_A/x_B \quad]$ and $[1/x_A \ln x_B /(1-x_A-x_B)x_{B\infty}H_B]$ versus $[\, x_B/x_A \,]$ give ε_{AA} (CH$_4$-CH$_4$ interaction) and ε_{BB} (CO$_2$-CO$_2$ interaction) from slope of line and CH$_4$-CO$_2$ (ε_{AB}) interaction gets from intercept.

RESULTS AND DISCUSSION

Plotting Adsorption Isotherms for CH$_4$/CO$_2$ Binary Mixture in Ono-Kondo Coordinates with Estimated Henry's Constants

Table 1 Dimensionless Henry's constants for adsorption of methane and carbon dioxide on activated carbon [17-19]

Adsorbate	H
T = 318 K	
Methane	60
Carbon Dioxide	100
T = 298 K	
Methane	45
Carbon Dioxide	74

Plotting Y (the first term in equations 4 and 5) as a function of x_A/x_B, we can get the value of ε_{AA} and ε_{BB} from the slope of the graph. The sign of $z_2\varepsilon_{AA}/kT$ and $z_2\varepsilon_{BB}/kT$ give information about the sign of adsorbate-adsorbate interactions. These coordinates also gives the intercept, $z_2\varepsilon_{AB}/kT$ which can be used to that verify this simplistic model is reasonable for gas-solid systems.

We used the equilibrium adsorption data for CH$_4$/CO$_2$ binary mixture on activated carbon Filtrasorb 400 at 318 K and pressures up to 13.6 MPa (calculated from ref. [20]) and on activated carbon Norit R1 Extra at 298 K (calculated from ref. [21]) to analyze adsorption isotherms.

Figures 2 and 3 illustrate adsorption isotherms for CH$_4$/CO$_2$ binary systems in coordinates of equations (4) and (5), respectively with the estimated H values in Table 1 [17-19]. The results for different systems (various concentration and different adsorbents) have similar shapes: the change of adsorbate-adsorbate interactions for CH$_4$/CO$_2$ mixture is similarly going down to a certain minimum and then going up. From Figures 2 and 3, compressed molecules can be occurred on both adsorbents at high concentrations with negative slope of line and the most of the scale of x_B/x_A over than x_A/x_B. This transition indicates the competitive nature of the individual component adsorption from the mixtures. CO$_2$ is most adsorbed component. Even if the concentration of CO$_2$ in the bulk is lowered, the adsorption competitive stays in favor of CO$_2$. The main reason for this behavior lies in the value of the fluid-solid interaction value, which is higher for CO$_2$ (-1427 K) as compared to CH$_4$ (-1122 K) [22].
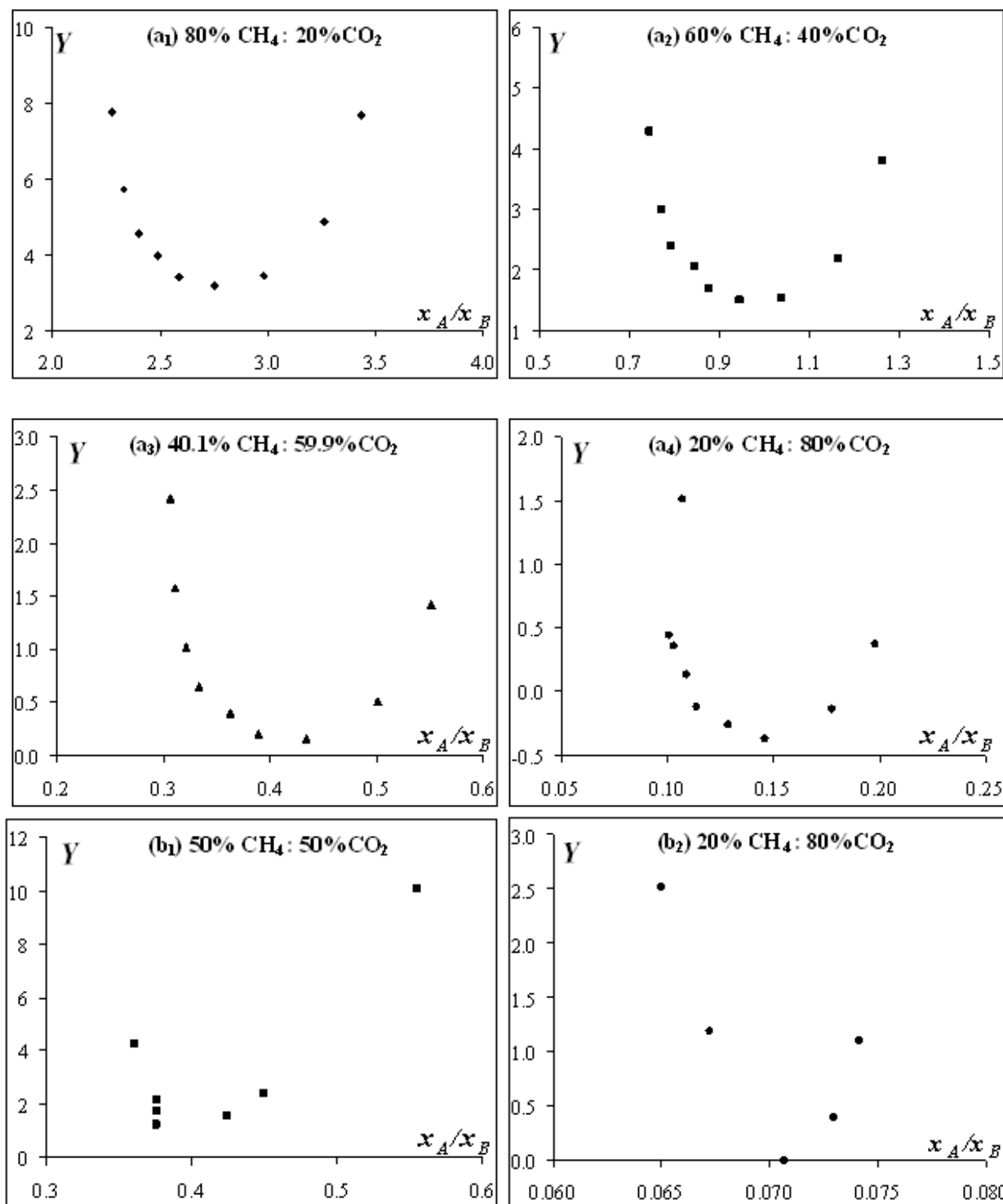
Figure 2 Adsorption isotherms in Ono-Kondo coordinate of equation (4): (a$_1$)-(a$_4$) for CH$_4$/CO$_2$ binary systems adsorbed on activated carbon Filtrasorb 400 at T = 318.2 K [calculated from ref. 20], and (b$_1$)-(b$_2$) for CH$_4$/CO$_2$ binary systems adsorbed on activated carbon Norit R1 Extra at 298 K [calculated from ref. 21]. Specified CH$_4$ is *A* component and CO$_2$ is *B* component.

From Figures 4 and 5, the results show the adsorption compression behavior at high pressure ends. High pressure ends are marked by circles and right frames give high pressure ends in much larger scales. These graphs allow estimates of energies of adsorbate-adsorbate repulsions in supercritical systems. Comparison of Figures 4 and 5 indicates adsorption compression of carbon dioxide is much stronger than methane that notice from larger scale of x_B/x_A.
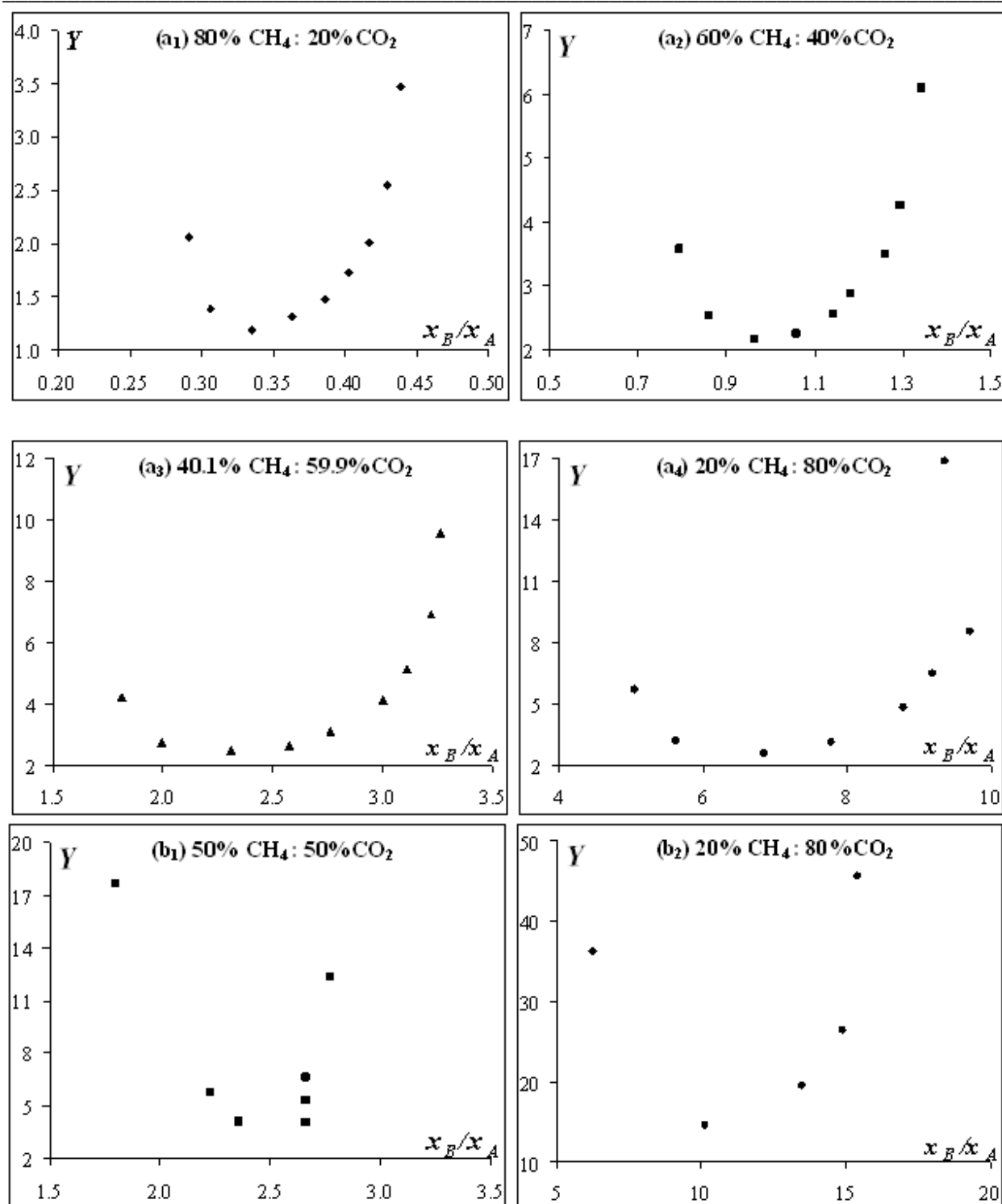
Figure 3 Adsorption isotherms in Ono-Kondo coordinate of equation (5): (a₁)-(a₄) for CH₄/CO₂ binary systems adsorbed on activated carbon Filtrasorb 400 at T = 318.2 K [calculated from ref. 20], and (b₁)-(b₂) for CH₄/CO₂ binary systems adsorbed on activated carbon Norit R1 Extra at 298 K [calculated from ref. 21]. Specified CH₄ is *A* component and CO₂ is *B* component.
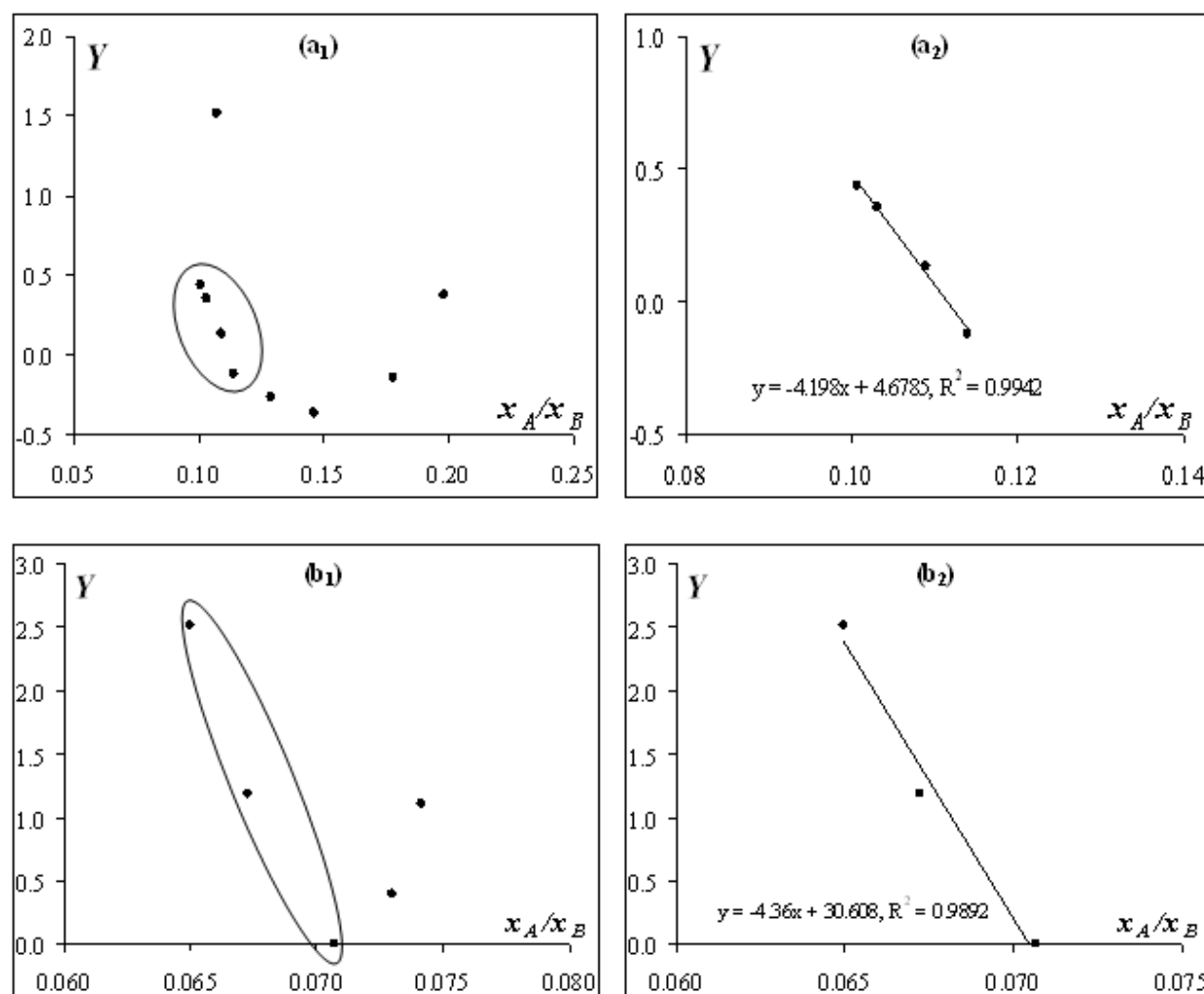
Figure 4 Adsorption isotherms in Ono-Kondo coordinate of equation (4): (a) for 20%CH_4 : 80%CO_2 binary mixture adsorbed on activated carbon Filtrasorb 400 at T = 318.2 K [calculated from ref. 20], and (b) for 20%CH_4 : 80%CO_2 binary mixture adsorbed on activated carbon Norit R1 Extra at 298 K [calculated from ref. 21]. Circles indicate high composition ends, and right frames show high composition ends in larger scale.

The negative slopes of lines (positive interaction energies) indicate repulsions between adsorbate molecules on the surface. These isotherms indicate the transition from attraction to repulsion between molecules of the adsorbate. The positive values of interaction energy are not surprising because of the very strong Lennard-Jones repulsion between adsorbed molecules on nearest neighbor adsorption sites. This also suggests that the repulsive part of adsorbate-adsorbate interactions is the dominant contribution to the average intermolecular interaction at high densities. Therefore, the adsorption compression behavior can be affected on the preferential adsorption of CO_2 over CH_4 at high pressure ends.
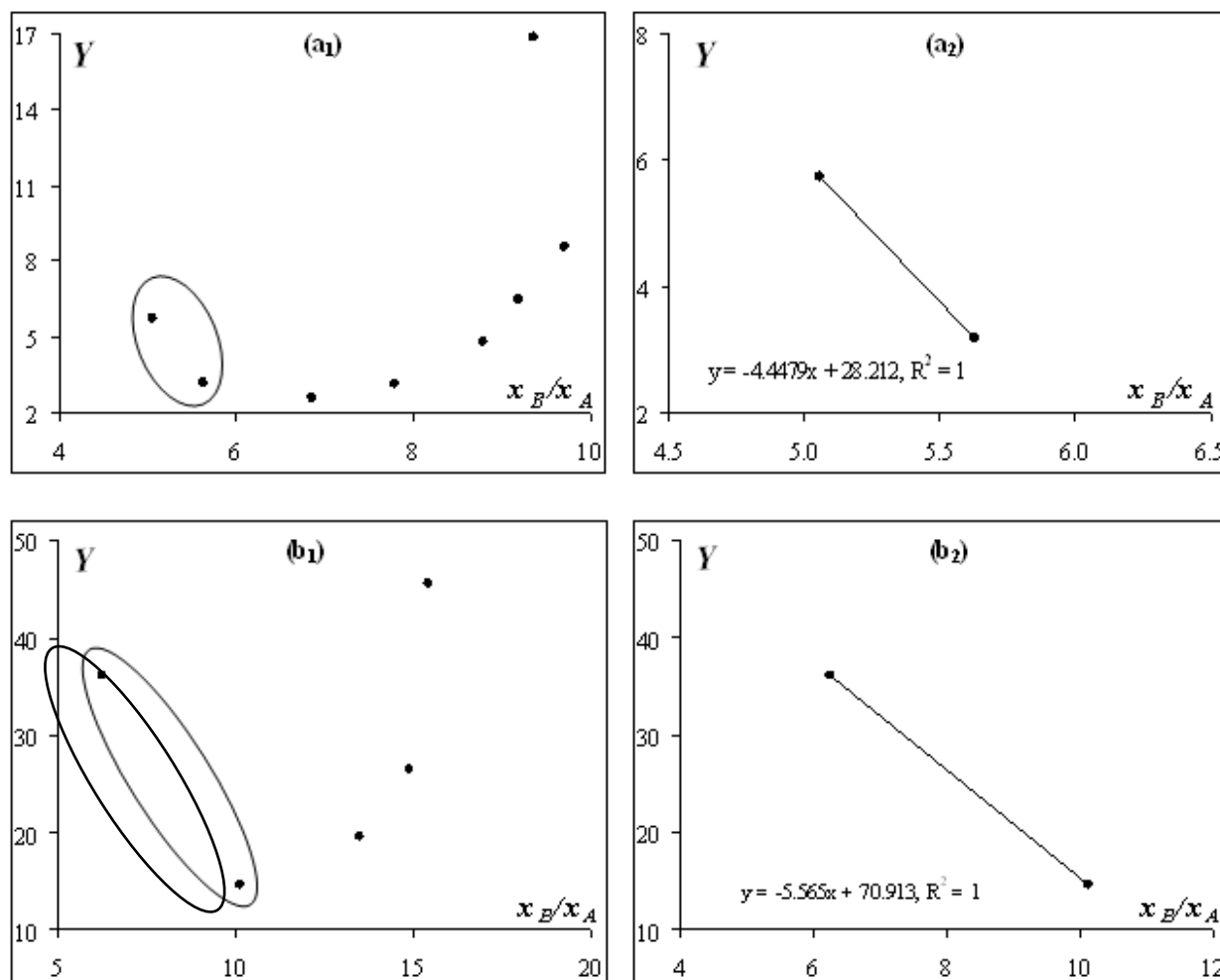
Figure 5 Adsorption isotherms in Ono-Kondo coordinate of equation (5): (a) for 20%CH$_4$: 80%CO$_2$ binary mixture adsorbed on activated carbon Filtrasorb 400 at T = 318.2 K [calculated from ref. 20], and (b) for 20%CH$_4$: 80%CO$_2$ binary mixture adsorbed on activated carbon Norit R1 Extra at 298 K [calculated from ref. 21]. Circles indicate high composition ends, and right frames show high composition ends in larger scale.

CONCLUSION

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.

Compressed molecules can be expected on any adsorbent at high concentrations where the adsorbed layer is nearly full. At high enough density, interactions in adsorbed layer become repulsive and ε_{AA}, or ε_{BB} (adsorbate-adsorbate interaction) becomes positive, but the total change in energy still can be negative because of large negative ε_s (adsorbate-adsorbent interaction). However, the repulsion of molecules in the full monolayer seems to be general behavior for high enough affinity to the adsorbent.

Therefore, adsorption compression can be occurred in binary systems where one of component has a high affinity to the surface of adsorbent. The strong field of the adsorbent pulls adsorbate molecules into surface phase at the density higher than in normal liquid which indicates repulsions between molecules in adsorbed phase under supercritical conditions.

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