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sII Structural Transitions from Binary Mixtures of Simple sI Formers[1]

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Previous work has shown structure II structural transitions for binary guest mixtures of simple structure I formers. This phenomenon was investigated using the hydrate statistical mechanical model developed by van der Waals and Platteeuw. Langmuir constants were employed to suggest that molecules at either extrema of the sI size range will form sII when mixed together. Thus, CO_2, an intermediate-sized sI former, was determined not to undergo a sII transition when combined with another sI former. Correlations between the Kihara potential parameters and physical properties were also made for pure hydrate formers.

KEY WORDS: binary hydrates; simple structure I formers; structural transitions.

1. INTRODUCTION

Clathrate hydrates are non-stoichiometric crystalline inclusion compounds consisting of a water framework which enclathrates, or traps, light molecules such as CH_4 and CO_2. The two common hydrate structures found in gas-processing and natural environments are structure I (sI) and structure II (sII) [1]. The unit cell of the sI hydrate (Pm3n, $a \approx 12\,\text{Å}$) consists of six large ($5^{12}6^2$) cages and two small (5^{12}) cages. This gives a ratio of 3:1 large-to-small cages. The unit cell of the sII hydrate (Fd3m, $a \approx 17\,\text{Å}$) consists of eight large ($5^{12}6^4$) cages and sixteen small (5^{12}) cages. This gives a

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ratio of 1:2 large-to-small cages. The different distribution of the cages in the two structures leads to sII containing 2.7 times more 5^{12} cages per unit volume then sI [2].

The hydrate structure with the lowest chemical potential (μ_w) will be the stable structure. The contributions to the water chemical potential are the hypothetical "empty" lattice (μ_w^β) and the reduction in the chemical potential due to the occupancy of the cages by guest molecules [3]. The sII hydrate is inherently more stable with a lower "empty" lattice chemical potential. At 273 K and 0 MPa, the "empty" lattice chemical potential relative to ice for sI is $302\,\text{cal}\cdot\text{mol}^{-1}$ while sII has a value of $211\,\text{cal}\cdot\text{mol}^{-1}$ [4]. This means that the decrease in μ_w^{sI} due to guest occupation of cages must be greater than that of μ_w^{sII}, in order for sI to form.

When only one guest is present, the guest size is the main factor in determining which hydrate structure will form. In simple hydrate systems (only one guest type), a molecule that is too large to fit in the $5^{12}6^2$ cages of sI will enter the $5^{12}6^4$ cage and sII will be the stable structure. Conversely, when a molecule's size is too small and can no longer stabilize the $5^{12}6^2$ cages, sII will be the stable structure because of the higher density of 5^{12} cages.

As far back as 1954, X-ray studies by Von Stackelberg and Jahns [5] showed that certain mixtures of H_2S and CH_3CHF_2 (both simple sI formers) formed sII hydrates. This result was later predicted by van der Waals and Platteeuw in 1959 [3]. The prediction tool was a statistical mechanical hydrate model developed, based on Langmuir adsorption of guests into the hydrate cages.

Another structural transition prediction using this hydrate model was reported by Hendriks et al. [6], in 1996, for binary systems of simple sI formers including $H_2S + C_2H_6$ and $CH_4 + C_2H_6$. The $CH_4 + C_2H_6$ structural transition was later verified experimentally by Subramanian et al. [7], who found that at 278 K, sII hydrate forms for methane compositions between 73 and 99 mol%.

These surprising results, both from prediction and experiment, have been discussed only briefly in the literature. From the work of van der Waals and Platteeuw, the sII transition in mixtures of simple sI formers was attributed to the greater number of small cages per unit volume in the sII hydrate [3]. Ripmeester [8] suggested that the sII transitions may occur in binary simple sI systems when one molecule is a large sI former that does not occupy the 5^{12} cage and one must strongly stabilize the small cage of both structures.

Hendriks et al. [6] showed that even a simplified approach used to model the fugacity as partial pressures for the $CH_4 + C_2H_6$ system predicted structural transitions. For the $CH_4 + C_2H_6$ system, a perturbation analysis was performed by adding a small amount of ethane to a methane system. This analysis showed the sII $5^{12}6^4$ cage had the greatest contribution to hydrate stability. A physical explanation was proposed that when the methane is present in low feed gas concentrations, methane and ethane compete for the large cages of the sI hydrate, while they cooperate at higher methane mole fractions to stabilize the sII hydrate. sII stabilization results because the small molecule, in this case methane, statistically favors occupation of the sII small cages due to the greater 5^{12} density in the sII framework.

2. PROCEDURE

In order to evaluate the stability of hydrate structures for various binary mixtures of simple sI formers, a computer hydrate program (CSMGem), developed by Ballard [9,10], was used that employs the van der Waals and Platteeuw (vdW & P) model. The prediction program, CSMGem, incorporates the vdW & P hydrate model along with performing a Gibb's energy minimization for all phases present in the flash.

The program uses the Kihara potential for calculation of Langmuir constants, which are a function of molecular attraction to a specific hydrate cage. Because of complications with the water in the lattice, viscosity and virial data are not sufficient for determining guest molecule Kihara parameters [1]. The Kihara parameters obtained for each molecule are calculated from a regression of experimental pressure and temperature data for hydrate formation. Only the hard-core radius (a) was determined using virial data. Figure 1 shows the Kihara pair potential, with its parameters labeled, versus intermolecular separation.

To evaluate the stable hydrate structure formed from binary systems of real and hypothetical simple sI formers, several steps were taken. First, two molecules were considered in the CSMGem framework with the same properties as methane, such as fugacity and water solubility. The product of the Langmuir constant and fugacity of the guest is the driving force for occupancy [11]. In this study, only the effects of the Langmuir constant were investigated by setting the fugacity of the two molecules equal to that of methane. Secondly, the hard-core radius was fixed at the value calculated for methane. With the hard-core radius fixed, an effective Kihara size parameter was used ($\sigma = \sigma^* + a$), where σ^* is the Kihara parameter that, in hydrates, is generally directly regressed from experimental data.

The sII transitions were determined to be a weak function of the Kihara well depth (ε). The main effect of ε was to change the compositional range for which the sII transition was predicted to occur. Because

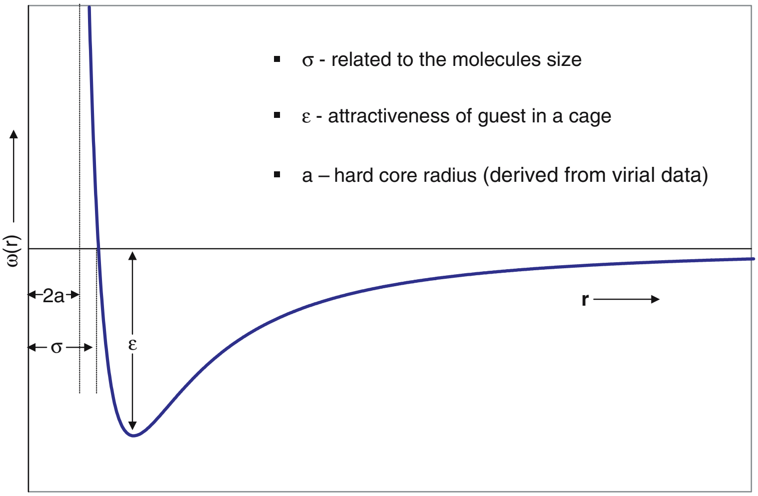

Fig. 1. Kihara pair potential versus intermolecular separation.

the focus of this study was to investigate only whether the sII transition would occur in particular binary systems, ε was held constant.

3. RESULTS

3.1. Simple Hydrate Formers

σ ($=\sigma^* + a$) [10] was plotted versus molecular radius for a number of molecules of various sizes. A linear correlation ($R^2 = 0.93$) was calculated as shown in Fig. 2. As molecular size increases, σ also increases. We note that the Kihara parameters were regressed primarily from experimental P-T data, without explicitly accounting for the guest molecule's size. The correlation is

$$\sigma = 0.4834 \text{ (molecular diameter/Å)} + 1.4696. \tag{1}$$

ε is the Kihara potential parameter that is related to the attraction of a molecule within a hydrate cage, or physically how well the guest can stabilize the hydrate cage. A decrease in dissociation pressure at constant temperature for different guests indicated increased hydrate stabilization. As shown in Fig. 3, ε/k [10] was plotted against experimental dissociation pressures for a set of molecules at around 273 K. Pressure data were obtained from the monograph by Sloan [1]. All the data were measured for three-phase ($V - L_W - H$) equilibrium.

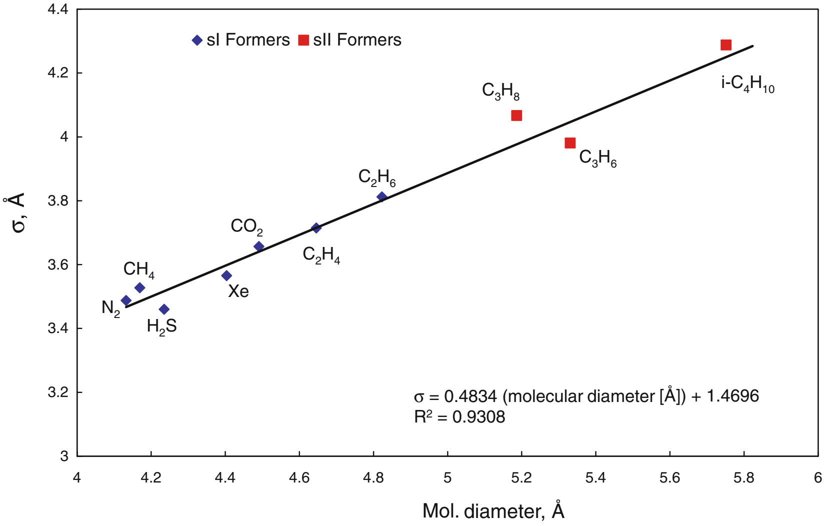

Fig. 2. Regressed σ values [10] versus molecular diameter.

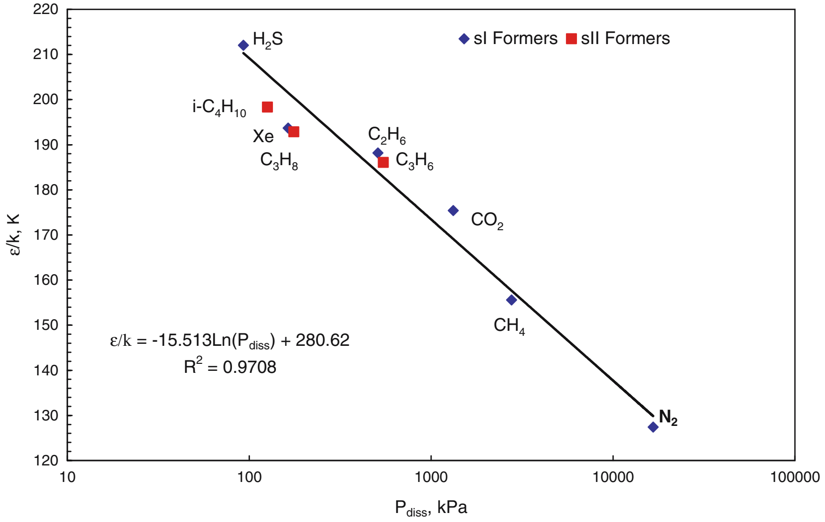

Fig. 3. Semi-logarithmic plot of regressed ε/k values [10] versus the hydrate's experimental $(V - L_w - H)$ dissociation pressure at around 273 K [1].

The semi-logarithmic fit of ε/k showed excellent agreement with the pressure stability data, even at the much higher dissociation pressures for N_2 ($R^2 = 0.97$). The correlation is

$$\varepsilon/k = -15.513\ln(P[\text{kPa}]) + 280.62. \tag{2}$$

The ability of a molecule to stabilize a cage appears to be directly related to the fit of a guest inside of the cage. Holder and Manganiello [12] reported that a value of σ/(hydrate cage diameter) = 0.44 was optimal. Comparison of this optimal ratio can be made with molecules such as H_2S and Xe to show that the guest-to-cage size ratio, not the size of the molecule alone, determines how well a molecule can stabilize a hydrate. H_2S is only slightly smaller than Xe, yet has a much lower dissociation pressure. While ε is not a size parameter, it is directly related to the guest size in relation to the hydrate cage it occupies.

Langmuir constants are calculated from the Kihara potential and are guest, hydrate cage specific. For each guest in a given hydrate structure, an average Langmuir constant ($C_{j,\text{avg}}$) can be defined as

$$C_{j,\text{avg}} = \frac{N_\text{s}C_{j,\text{S}} + N_\text{L}C_{j,\text{L}}}{\textit{no.cages per unit cell}}, \tag{3}$$

where j is the hydrate structure, $C_{j,\text{S}}$ and $C_{j,\text{L}}$ are the Langmuir constants for molecule j in the small and large cages, N_S and N_L are the number of small and large cages per unit cell. If $C_{j,\text{avg}}$ is plotted versus the experimentally regressed values of ε, a strong exponential trend ($R^2 = 0.97$) can be seen for simple sI formers. In Fig. 4, this trend is present for the sI formers. Because the sI $C_{j,\text{avg}}$ is slightly greater than that of sII, sI is stabilized preferentially for molecules shown in Figure 4.

This $C_{j,\text{avg}}$ analysis was extended to simple sII formers, in Fig. 5, showing a strong correlation ($R^2 = 0.99$) between the $C_{j,\text{avg}}$ for three simple sII formers and ε.

By setting ε and the hard-core Kihara parameters, Langmuir constants at a given temperature can be calculated as a function of only σ for each hydrate cage, similar to the approach used in Ref. 12. In Figure 6, the regressed σ for ethane is marked by a vertical line at $\sigma = 3.43$ Å. The Langmuir constant for ethane in the $5^{12}6^2$ and the $5^{12}6^4$ cages are approximately the same. The Langmuir constant for ethane in the 5^{12} cages of both structures is small and considered negligible. Ethane, as a simple former, forms sI hydrate, a fact attributed to the greater large cage density in the sI hydrate versus the sII hydrate.

A similar plot to Fig. 6 using the parameters for methane is shown in Fig. 7. σ for methane (3.14 Å) is shown as a vertical line. Methane

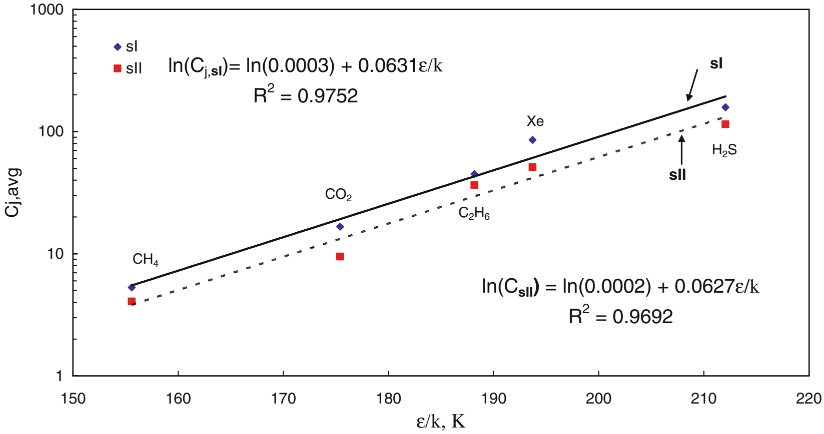

Fig. 4. $C_{j,\mathrm{avg}}$ versus ε/k calculated for both sI and sII hydrate with simple sI formers.

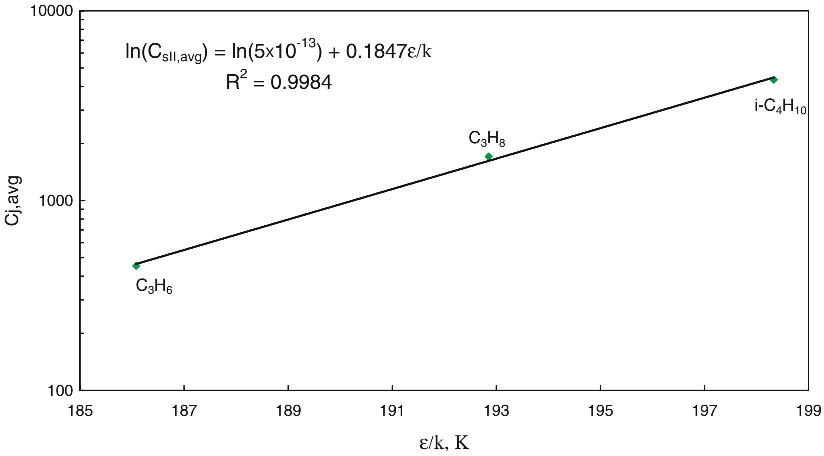

Fig. 5. $C_{j,\mathrm{avg}}$ versus ε/k calculated for sII hydrate with simple sII formers.

stabilizes the 5^{12} cages of both structures almost equally, but the Langmuir constant is slightly larger for the 5^{12} of sI. The Langmuir constant for methane in the $5^{12}6^{2}$ cage is greater than that in the $5^{12}6^{4}$ cage. Higher Langmuir constant values in both cages show why sI is the stable structure for methane.

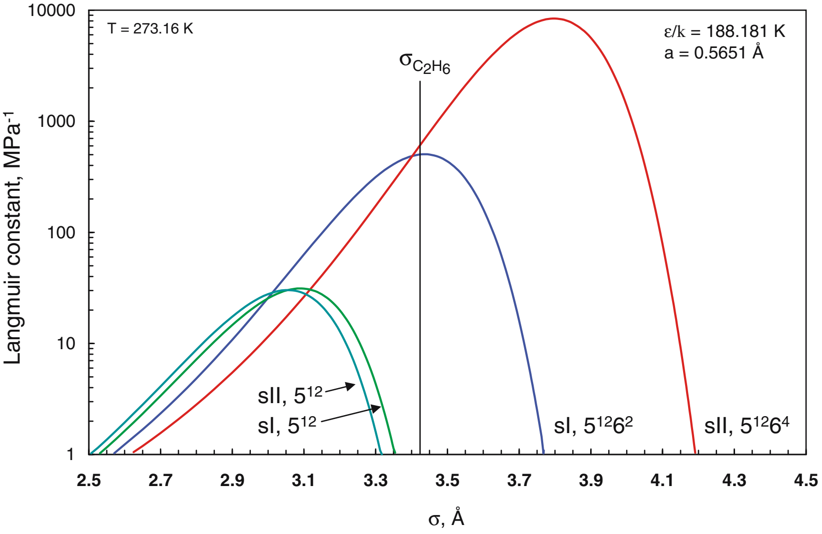

Fig. 6. Langmuir constant [MPa^{-1}] versus σ for ethane ($\varepsilon/k = 188.181$ K).

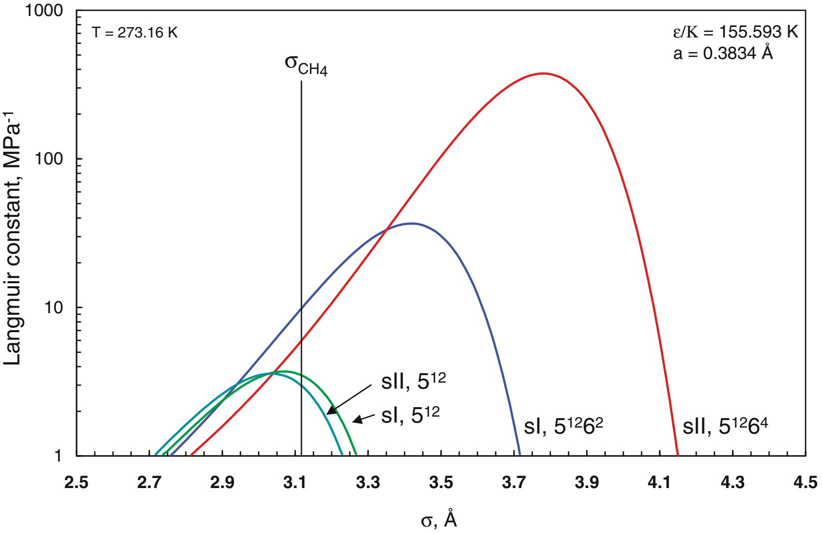

Fig. 7. Langmuir constant [MPa^{-1}] versus σ for methane ($\varepsilon/k = 155.593$ K).

3.2. Binary Guest Hydrate Formers

Using CSMGem with two pseudo-methane molecules described above, we determined that certain size conditions must exist for a sII structural transition to occur from a binary mixture of simple sI formers. First, the "small" molecule was set to the lowest value of σ that produced a simple sI hydrate (3.11 Å). The size, or σ, of the "large" molecule was varied over the range of σ for a simple sI hydrate.

With the "small" molecule set at the lower σ limit for simple sI formation, a sII transition was found to exist for σ values of the large molecule from 3.33 to 3.43 Å, where 3.43 Å is the maximum for simple sI formation. This "large" molecule range is shown in Fig. 8a as a checkerboard box. Using Eq. (1), with the "small" molecule having a radius of 4.19 Å, the "large" molecule with a size ranging from 4.64 to 4.85 Å will form sII hydrate over a certain compositional range.

Also, for a sII binary transition to exist, a similar lower sI range exists if the "large" molecule is at the upper sI size limit. Thus, a molecule of $\sigma = 3.43$ Å can combine with a "small" molecule with σ = 3.11–3.21 Å to form sII hydrate over a certain compositional range.

If the "small" molecule's σ is slightly greater than 3.11 Å, then the "large" molecule's sI σ range, in which a sII transition occurs, decreases. For example, if the small molecule has σ = 3.16 Å, then the upper size range reduces to $\sigma = 3.39$–3.43 Å. The decrease in the "large" molecule range is shown in Fig. 8b as a checkerboard box. If the "large" molecule's σ is slightly less then 3.43 Å, the lower sI σ range, for sII transitions, decreases. For example, if the "large" molecule has σ = 3.38 Å, then the lower size limit is from $\sigma = 3.11$–3.15 Å.

In the case of carbon dioxide, which is an intermediately sized simple sI former, there is no upper or lower range for a second simple sI forming guest in which a sII transition occurs. Figure 8 shows the size of carbon dioxide overlaid on a plot of Langmuir constants calculated for the Kihara parameters for carbon dioxide. Experimentally, no compositionally dependent sII transition has been reported for systems such as $CH_4 + CO_2$ [13], nor is a sII transition predicted for binary mixtures of CO_2 with larger molecules, such as C_2H_6, via the above reasoning.

4. CONCLUSIONS

The regressed Kihara hydrate parameters, representing the body of experimental *P-T* data, have been related to physical parameters. σ, which is the Kihara size parameter, is proportional to molecular size. The ε parameter varies inversely with dissociation pressure at a given

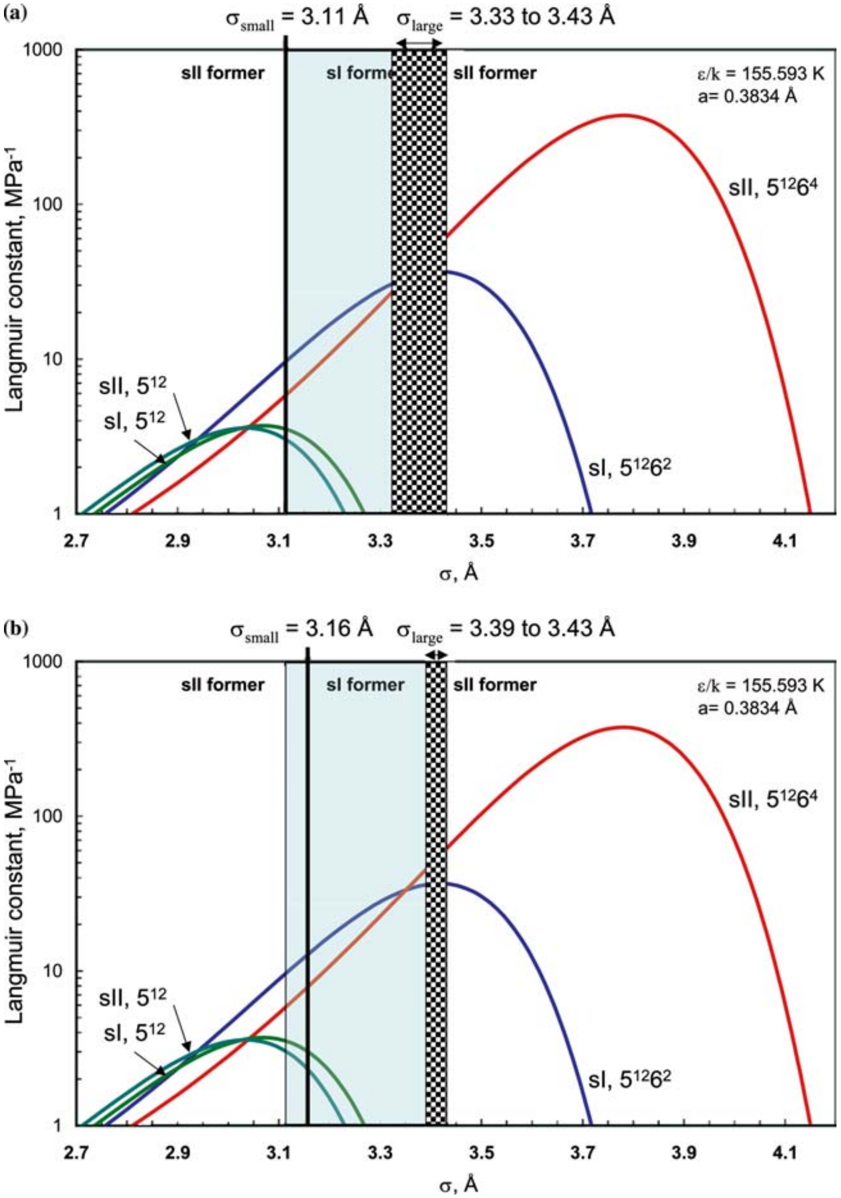

Fig. 8. (a) Langmuir constants for molecule in the various cages of sI, sII hydrate ($\varepsilon/k = 155.593\,\mathrm{K}$, $a = 0.3834\,\text{Å}$). σ of the small molecule is 3.11 Å. The region for a sII transition when mixed with a "large" sI former is between $\sigma = 3.33$ and 3.43 Å (shown by checkerboard box). (b) Langmuir constants for molecule in the various cages of sI, sII hydrate ($\varepsilon/k = 155.593\,\mathrm{K}$, $a = 0.3834\,\text{Å}$). σ of the small molecule is increased to 3.16 Å. The region for a sII transition when mixed with a "large" sI former decreases to between $\sigma = 3.39$ and 3.43 Å (shown by checkerboard box).

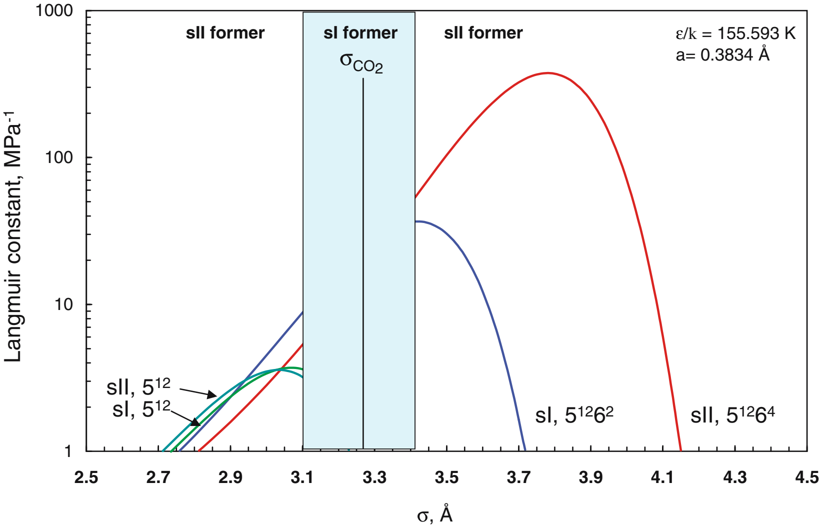

Fig. 9. Langmuir constants for CO_2 in the various cages of sI, sII hydrate. The size of $CO_2$is in the intermediate range of simple sI formers.

temperature such as 273 K. That is, an increase in ε indicates an increasingly stable hydrate will form.

When combining CH_4 with C_2H_6, it is known that a sII transition occurs. Because CO_2 is in the intermediate size range of simple sI formers, it can be mixed with no other simple sI molecule to form a sII hydrate.

Size difference between two simple sI formers determines if a sII transition exists. A quantitative analysis of sII transitions has been presented. One molecule must effectively stabilize the small (5^{12}) cage in either structure, while the other molecule must effectively stabilize the large (5^{12} 6^2 or 5^{12} 6^4) cages. This has been shown to occur when one molecule of the binary mixture is near the lower limit of sI formation and the other is near the upper limit of sI formation. This analysis, also, is in agreement with other predictions that systems such as $H_2S + C_2H_6$ should have a compositely dependent sII transition.

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