Utilization of "Instantaneous Molecule Cluster (IMC)" Hypothesis to Predict VLE in CO_2 Absorption by Alkanes

Tang Zhi-Gang, Li Hong-Wei, Chen Jian, Guo Dong, and Cui Jing-Jie

***Abstract*—In this paper, "Instantaneous Molecule Cluster (IMC)" hypothesis is used to predict the VLE in CO_2 absorption by alkanes. It is shown that the predicted values are satisfied with the experimental values (cited data) well. The results also reveal that the effect of homogenous instantaneous molecule cluster among the alkane molecules is the key factor. As carbon chain elongation, formation probability and stability of the instantaneous molecule cluster decreases and absorption capacity increases. The impact of parameter on VLE is also discussed in this paper.**

***Index Terms*—Alkane, CO_2 absorption, instantaneous molecule cluster, VLE.**

I. Introduction

In recent years capture of CO_2 becomes a hot-spot due to severely global climate change caused by greenhouse gas emission. Absorption method gets more and more researcher's attention on account of its advantages as mature, high reliable and prone to realization in engineering. One of important branches is how to predict the VLE in CO_2 absorption. At present, some predicted models such as Scatchard-Hildebrand Model [1], [2] Prausnitz-Shair Model [3] which are both based on regular solution theory, and other improved model, based on the above methods, such as Yen-Mcketta Model [4], [5] have been reported.

According to Prausnitz-Shair theory, dissolution of gas in liquids consists of two steps: (1) gas solute "condenses" at a certain temperature and becomes a virtual liquid with liquid-like volume; (2) "condensed" virtual liquid dissolves in solvent and becomes solution. It also provides the methods to calculate the activity coefficient and solubility of gas dissolved in solvent as the following [1], [2]:

$$\ln \gamma_i = \frac{V_i(\delta_i - \delta_s)^2}{RT}\Phi_s^2 \tag{1}$$

$$\ln \gamma_s = \frac{V_s(\delta_i - \delta_s)^2}{RT}\Phi_i^2 \tag{2}$$

$$\ln x_i = \ln(\frac{1}{f_i}) - \frac{V_i}{RT}(\delta_s - \delta_i)^2 \tag{3}$$

where, γ_i activity coefficient of gas solute in solution; γ_s activity coefficient of solvent in solution; V_i molar volume of virtual liquid, $m^3\ mol^{-1}$; V_s molar volume of solvent, $m^3\ mol^{-1}$; δ_i solubility parameter of virtual liquid, $MPa^{1/2}$; δ_s solubility parameter of solvent, $MPa^{1/2}$; Φ_i volume fraction of virtual liquid; Φ_s volume fraction of solvent; f_i^l fugacity of virtual liquid, MPa; x_i solubility of gas dissolved in solvent at a certain temperature, molar fraction;

Prausnitz-Shair method and its improvements predict the solubility of gas depends on calculation of activity and does not take into account the interaction between molecules. It makes its application to interpret the solute-solvent interaction and solution structure had significant limitations.

Based on activity coefficient equation or state equation, the prediction of the above model has high accuracy, but requires extensive calculation. What is more, the prediction of phase equilibrium always needs such a "black box"-activity coefficient as a bridge, which lacks of a clear image of the interaction mechanism and solution structure during the absorption process.

Instead of activity coefficient method with complex and tedious calculations, "Instantaneous Molecule Cluster (IMC)" hypothesis is proposed, based on a hypothesis about interaction mechanism among solute molecules-solute molecules, solute molecules- solution molecules, and solution molecules-solution molecules. Zhigang Tang *et al* [6] had used IMC hypothesis to interpret the causes of azeotropic phenomenon well. Binary VLE of acetic formic acid-water, acid-water and propionic acid-water was predicted satisfied by quantitative analysis. According to deduction of IMC, this hypothesis model in principle can be applied in all VLE prediction.

In this paper IMC hypothesis is used to interpret the interaction mechanism and VLE in absorption of CO_2 by alkanes. The impact of IMC parameters is also discussed.

II. Procedure for Paper Submission

According to IMC hypothesis [6], gas pressure above the V-L interface, when CO_2 absorption reaches the equilibrium, can be expressed by (4):

$$P_{AB} = P_A^S x_A + P_B^S x_B = P_A^S \frac{[A]}{[A] + k_A[A]^a + [B] + k_B[B]^b + k_{AB}[A]^m[B]^n} + P_B^S \frac{[B]}{[A] + k_A[A]^a + [B] + k_B[B]^b + k_{AB}[A]^m[B]^n} \tag{4}$$

where, A denotes CO_2, B denotes solvent; [A], [B] represents the molar concentration (mol/L) of CO_2 molecules and solvent molecules in solution, respectively; P^S_A, P^S_B is ideal vapor pressure of CO_2 and solvent; P^0_A, $P^0_B$are the saturated

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vapor pressure of CO_2 and pure solvent. The relation of P^S_A, P^S_B and P^0_A, P^0_B can be expressed by (5):

$$P_A^0 = \frac{P_A^S}{1+\frac{[A_a]}{[A]}} = \frac{P_A^S}{1+k_a[A]^{a-1}}$$
$$P_B^0 = \frac{P_B^S}{1+\frac{[B_b]}{[B]}} = \frac{P_B^S}{1+k_b[B]^{b-1}} \quad (5)$$

It can be seen that just when k_A or k_B is very small, the probability of IMC formation is extremely low, ideal vapor pressure and the saturated vapor pressure of pure solvent are very close.

Because CO_2 is gaseous at room temperature, P^0_A is taken values as liquefaction pressure of CO_2 at 25 ℃ with P^0_A=6586KPa; P^0_B is the saturated vapor pressure of alkanes, used as the absorbents in this paper, shown in Table I [7].

TABLE I: SATURATED VAPOR PRESURE VALUES OF THE ALKANES IN THIS PAPER [8]

Name	hexane	heptane	heptane	nonane	decane	undecane
P^0_B, kPa	20.43	6.065	1.859	0.5567	0.1809	0.0585

In (6) and (7), k_A, k_B represents the dynamic equilibrium constants of homo instant molecule cluster (HO-IMC) and A_a, B_b is molar concentration of HO-IMC. k_{AB} represents the dynamic equilibrium constants of hetero instant molecule cluster (HE-IMC) and A_m, B_n is molar concentration of HO-IMC, according to (8).

$$aA \overset{k_A}{\Leftrightarrow} A_a \quad (6)$$

$$bB \overset{k_B}{\Leftrightarrow} B_b \quad (7)$$

$$mA + nB \overset{k_{AB}}{\Leftrightarrow} A_mB_n \quad (8)$$

By above (6)- (8), $k_A[A]^a$, $k_B[B]^b$ and $k_{AB}[A]^m[B]^n$ in (4) actually equals to moral concentration of HO-IMC A_a、B_b, and HE-IMC A_mB_n, respectively. Parameter a, b represent statistical average (can be taken non-integer values, refer to [6]) values of single CO_2 molecule number and single absorbent molecule number to form HO-IMC according to (6) and (7). Parameter m, n represent statistical average values (also can be taken non-integer values, refer to [6]) of single CO_2 molecule number and single absorbent molecule number to form HE-IMC according to (8).

x_A, x_B in (4) represent molar fraction of CO_2 and absorbent in the form of single molecule in solution. In fact, CO_2 and solvent in solution exist in several forms as single molecules, HO-IMC and HE-IMC. So total mole fraction of CO_2 in all forms is written as

$$X_{AT} = \frac{[A]+a[A_a]+m[A_mB_n]}{[A]+a[A_a]+m[A_mB_n]+[B]+b[B_b]+n[A_mB_n]} \quad (9)$$

Using alkanes as absorption solvent, P_A and X_{AT} can be expressed by Henry equation according to experiments [8]:

$$P_{AB} = HX_{AT} \quad (10)$$

In this paper, the IMC hypothesis is tried to predict VLE on CO_2 absorption by alkanes and the reasonable values of parameter a, b, m, n, k_A, k_B, and k_{AB} in the above model is fitted.

III. PREDICTION OF THE VLE IN CO_2 ABSORPTION BY ALKANESBASED ON IMC HYPOTHESIS

Based the experimental results [8], Henry's constants of CO_2 in alkane are listed in Table II.

The least square method was applied to fit alkane cited data in Table II and the fitting values of a, b, m, n, k_A, k_B, and k_{AB} are listed in Table III with linear coefficients no lower than 0.99.

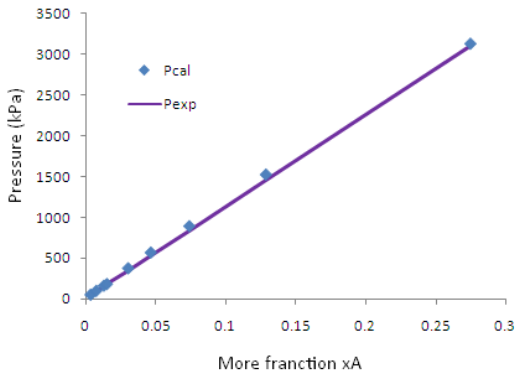
Based on data in Table III, the solubility of fitting values and cited data are plotted in Fig. 1. Where, the abscissa represents gas phase pressure above the V-L interface (kPa). The ordinate represents molar fraction of CO_2 in all forms in the liquid.

TABLE II: HENRY'S CONSTANT OF CO_2 IN ALKANES (25℃) [8]

Name	hexane	heptane	octane	nonane	decane	undecane
Henry's constant(MPa)	11.334	8.8736	8.4879	7.2728	5.7253	5.0513

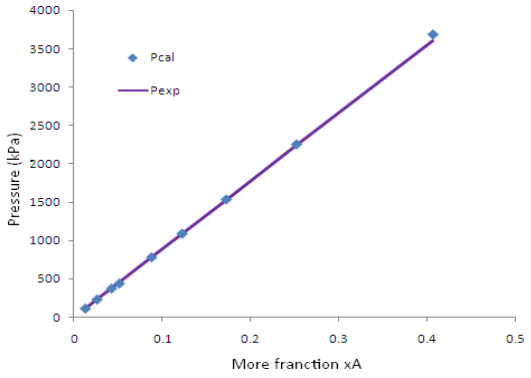
TABLE III: FITTING VALUES OF IMC PARAMETERS IN THIS PAPER

Name	hexane	heptane	octane	nonane	decane	undecane
a	1.8~2.1	1.8~2.1	1.8~2.1	1.8~2.1	1.8~2.1	1.8~2.1
k_A	0.03~0.05	0.03~0.05	0.03~0.05	0.03~0.05	0.03~0.05	0.03~0.05
b	1.1~1.3	0.75~0.95	0.7~0.8	0.6~0.7	0.45~0.55	0.45~0.55
k_B	20~50	10~50	10~40	10~30	10~20	10~18
m ,n	little effect	little effect	little effect	little effect	little effect	little effect
k_{AB}	0~1.8	0~0.9	0~0.5	0~0.3	0~0.2	0~0.15



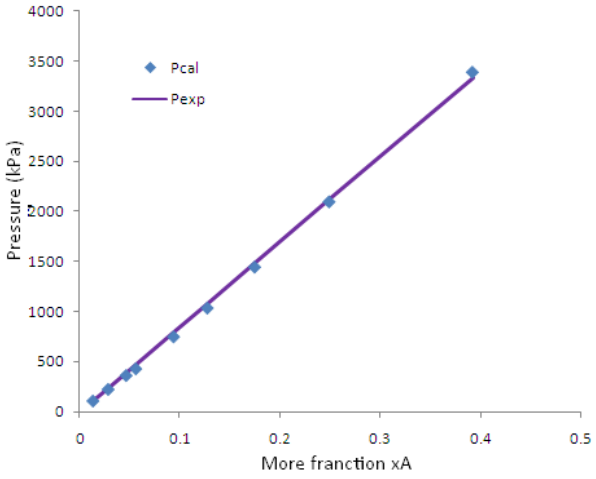
(a) hexane

(a=1.95, k_A=0.04, b=1.2, k_B=35, m=1, n=2, k_{AB}=0.9)



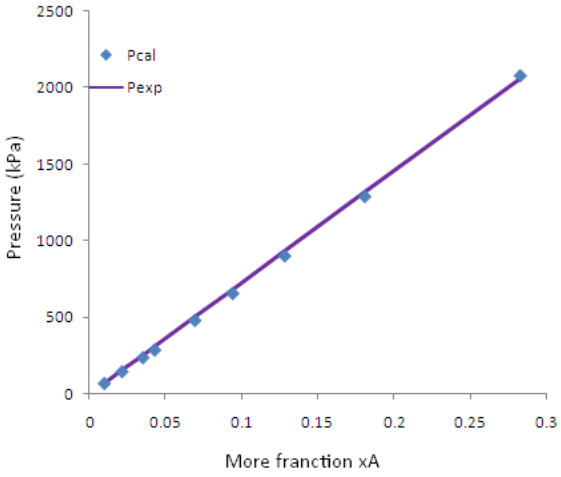
(b) heptane

(a=1.95, k_A=0.04, b=0.85, k_B=30, m=1, n=2, k_{AB}=0.45)



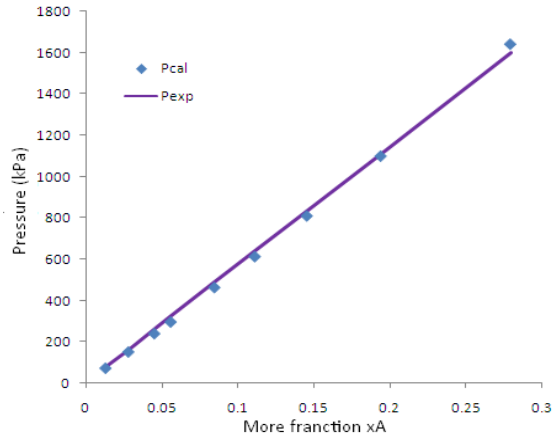
(c) octane

(a=1.95, k_A=0.04, b=0.75, k_B=25, m=1, n=2, k_{AB}=0.25)



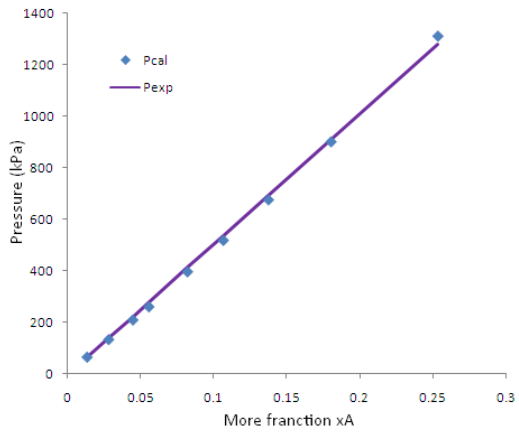
(d) nonane

(a=1.95, k_A=0.04, b=0.65, k_B=20, m=1, n=2, k_{AB}=0.15)



(e) decane

(a=1.95, k_A=0.04, b=0.5, k_B=15, m=1, n=2, k_{AB}=0.1)



(f) undecane

(a=1.95, k_A=0.04, b=0.5, k_B=14, m=1, n=2, k_{AB}=0.08)

Fig. 1. Comparison of solubility fitting values by IMC model and cited data [9] (25℃), (♦Pcal, fitting values by IMC model, — Pexp, cited data according to [9])

Seen Fig. 1, the fitted values by IMC and cited data coincides well (To make a convenient to plot, a, b, k_A, k_B, and k_{AB} in Fig. 1 are all taken average values of the feasible interval in Table III. As m and n have little impact on results during a wide range, m and n takes 1 and 2 in the above work.

It can be found that during the fitting range of parameters in Table III, the homogenous molecular interactions, especially solvent molecules interactions have a great influence on CO_2 absorption, which is proved by the fact that k_B is far greater than k_A and k_{AB}. By comparison of k_A, k_B, and k_{AB}, it is apparent that molecular interactions of CO_2 molecules are weakest and HO-IMC formation probability of CO_2 molecules is low. But HO-IMC stability of CO_2 is good, which can be observed by that the value of parameter a is in the range of 1.8 to 2.1. As k_B value is the biggest, HO-IMC formation probability of alkanes absorbent is the greatest but

HO-IMC stability is bad, which can be observed by that the value of *b* is small. Because the interactions between CO_2 molecule and solvent molecule are weak (k_{AB} is little), HE-IMC formation probability is small and impact of HE-IMC could be negligible on absorption results (*m* and *n* has a small impact on phase equilibrium within a wide range).

As mentioned before, there are differences between ideal vapor pressure and actually saturated vapor pressure of solvent according to IMC hypothesis. Based on fitting parameters of the above, ideal vapor pressure of alkane solvents used in this paper is listed in TABLE IV.

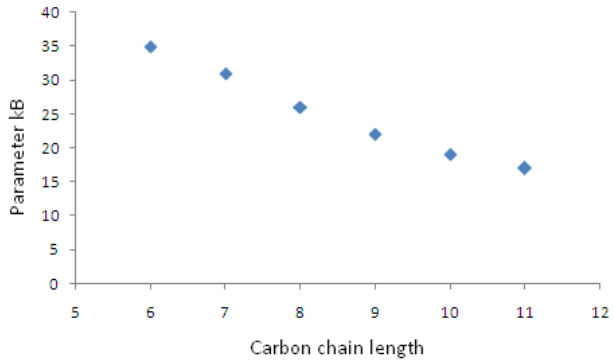
Traditional Prausnitz-Shair equation has prediction accuracy of about -30%~+30%. The improved Prausnitz-Shair equation may increase the accuracy to -10%~+10%. By IMC hypothesis, the prediction accuracy is about -10%~+10% similar with that of improved Prausnitz-Shair method.

Fig. 2 shows that changing tendency of parameter *b*, k_B and k_{AB} with carbon chain length of alkane absorbent. To make a convenient to plot, *a*, *b*, k_B ,and k_{AB} in Fig. 2 take average values from the fitting range of parameters in Table III. In Fig. 3, abscissa Cn represents carbon chain length of alkane absorbent (number of carbon atoms).

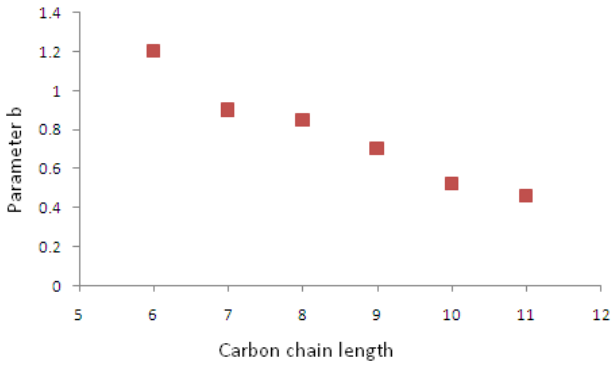
TABLE IV: IDEAL VAPOR PRESSURE AND SATURATED VAPOR PRESSURE OF ALKANES USED IN THIS PAPER

Name	hexane	heptane	heptane	nonane	decane	undecane
Saturated vapor pressure (kPa)	20.43	6.065	1.859	0.5567	0.1809	0.0585
b	1.2	0.85	0.75	0.65	0.5	0.43
ideal vapor pressure (kPa)	505.78	155.92	47.609	15.012	7.2378	4.8162

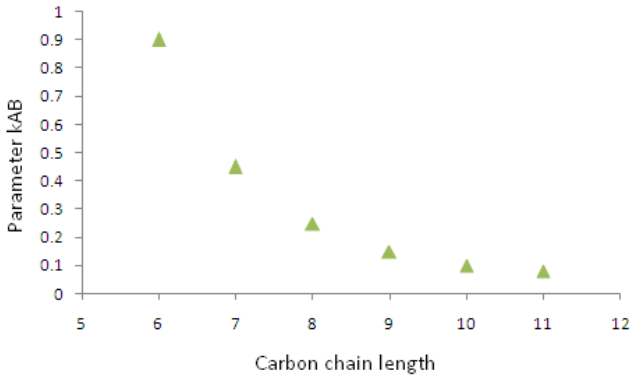
b is taken average values of the feasible interval in Table III



(a) k_B versus carbon chain length



(b) *b* versus carbon chain length



(c) k_{AB} versus carbon chain length

Fig. 2. *b*, k_B and k_{AB} change over alkane carbon chain length (25℃)

In Fig. 2, as carbon chain elongating, k_B decreases, which mean that interaction among absorbent molecules and HO-IMC formation probability reduce. Decreasing of *b* with carbon chain elongation (*b* is almost less than 1 when number of carbon atoms exceeds 7) illustrates stability of HO-IMC is getting worse. What is more, a gradual reduction in k_{AB} values shows that interactions between CO_2 molecule and alkane molecule are weaker and weaker, and HE-IMC formation probability falls gradually. Because k_{AB} is small, it can be negligible that impact of HE-IMC on absorption results.

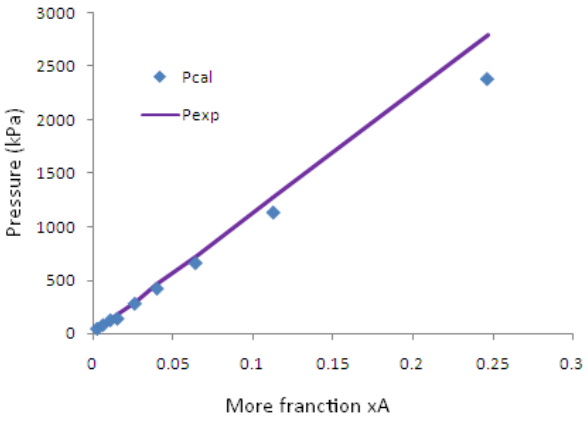
IV. EXTENDED DISCUSSION OF CO_2 ABSORPTION BASED ON IMC HYPOTHESIS

In order to reveal the mechanism of CO_2 absorption based on IMC hypothesis further, takes hexane as an example absorbent and discuss the influence of k_A, *a*, k_B, *b*, k_{AB}, *m*, and n on VLE in CO_2 absorption in the following.

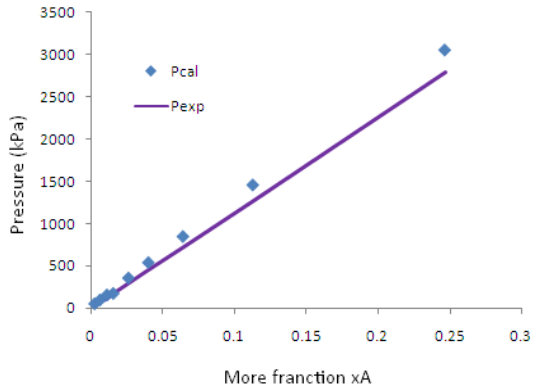
A. *Influence of* k_A

In the case of other parameters unchanged, as k_A decreases, the predicted values are gradually smaller than the

experimental values (cited data from [8]). However, as k_A increases, the predicted values are gradually larger than the experimental values (cited data from [8]), as shown in Fig. 3. The predicted values represent good agreement with the experimental values in a range of 0.02 to 0.06 for k_A. Thus it can be seen that interactions among CO_2 molecules are very weak.



(a=1.95, k_A=0.01, b=1.2, k_B=35, m=1, n=2, k_{AB}=0.9)



(a=1.95, k_A=0.07, b=1.2, k_B=35, m=1, n=2, k_{AB}=0.9)

Fig. 3. The impact of k_A on CO_2 absorption by hexane (25℃)

B. Influence of a

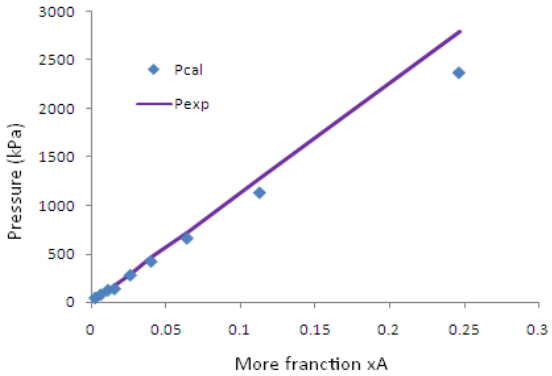
In the case of other parameters unchanged, as a decreases, the predicted values are gradually smaller than the experimental values (cited data from [8]). On the contrary, as a increases, the predicted values are gradually larger than the experimental values (cited data from [8]), as shown in Fig. 4.

It is worth noting, although homo interactions among molecules are very weak, HO-IMC stability is good. HO-IMC of CO_2 is roughly formed by two single CO_2 molecules. But HO-IMC concentration is relatively low. The predicted values represent good agreement with the experimental values in a range of 1.8 to 2.2 for a.

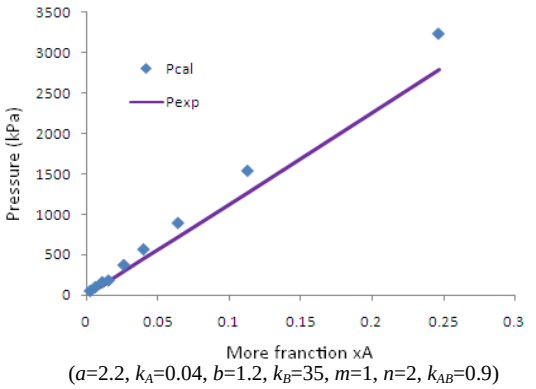
C. Influence of k_B

Similarly, in the case of other parameters unchanged, as k_B decreases, the predicted values are gradually smaller than the experimental values (cited data from [8]). However, as k_B increases, the predicted values are gradually larger than the experimental values (cited data from [8]), as shown in Fig. 5.

This situation may illustrate that interactions among hexane molecules are stronger than that among CO_2 molecules and HO-IMC formation probability of hexane molecules is bigger. k_B is chosen in a range of 20 to 50, and the predicted values represent good agreement with the experimental values.

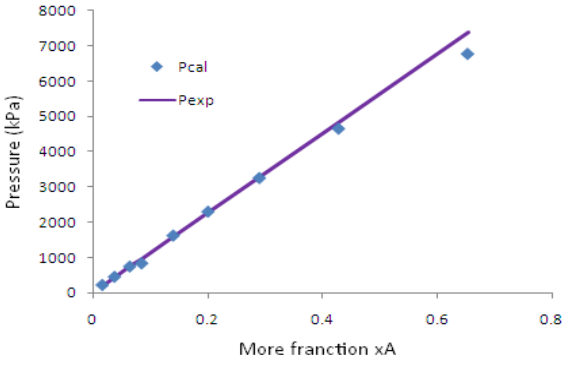


(a=1.7, k_A=0.04, b=1.2, k_B=35, m=1, n=2, k_{AB}=0.9)

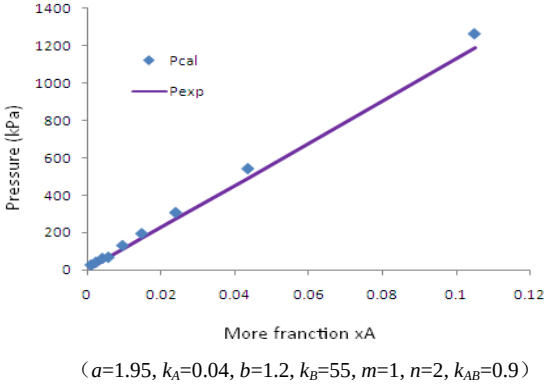


(a=2.2, k_A=0.04, b=1.2, k_B=35, m=1, n=2, k_{AB}=0.9)

Fig. 4. The impact of a on CO_2 absorption by hexane (25℃)



(a=1.95, k_A=0.04, b=1.2, k_B=15, m=1, n=2, k_{AB}=0.9)



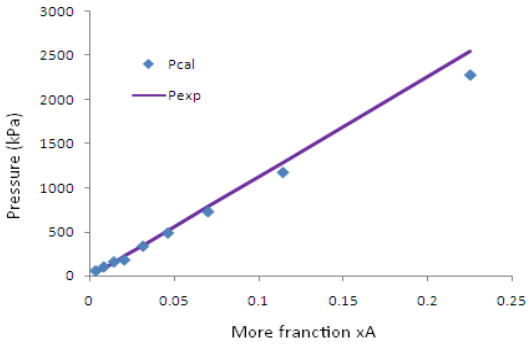
（a=1.95, k_A=0.04, b=1.2, k_B=55, m=1, n=2, k_{AB}=0.9）

Fig. 5. The impact of k_B on CO_2 absorption by hexane(25℃)

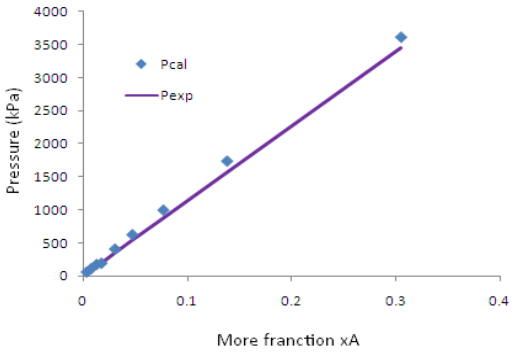
D. Influence of b

Keeping the other parameters unchanged, as *b* decreases, the predicted values are gradually smaller than the experimental values (cited data from [8]). However, as *b* increases, the predicted values are gradually larger than the experimental values (cited data from [8]), as shown in Fig. 6.

Because *b* is small, stability of hexane HO-IMC is bad. As carbon chain elongation, IMC stability of alkane system decreases gradually. The predicted values make a good agreement with the experimental values (cited data from [8]) in a range of 1.1 to 1.3 for *b*.



（a=1.95, k_A=0.04, b=1.0, k_B=35, m=1, n=2, k_{AB}=0.9）

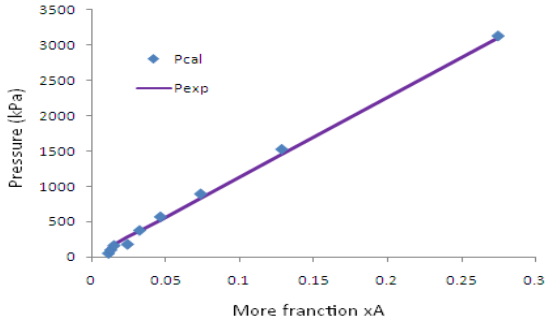


（a=1.95, k_A=0.04, b=1.4, k_B=35, m=1, n=2, k_{AB}=0.9）

Fig. 6. The impact of *b* on CO_2 absorption by hexane(25℃)

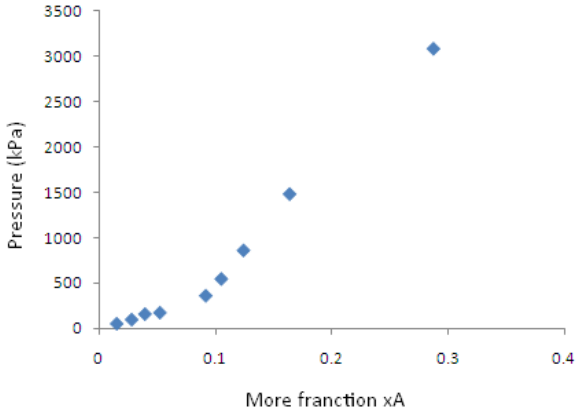
E. Influence of k_{AB}, m and n

When k_{AB} is large, deviations between predicted values and experimental values are distinct in low concentration area, as shown in Fig. 7. When k_{AB} is less than 0.9 (should be greater than zero), a good agreement is obtained. It shows that in CO_2 absorption by hexanes, interactions between hexane molecule and CO_2 molecule are weaker than that among hexane molecules, but stronger than that among CO_2 molecules.

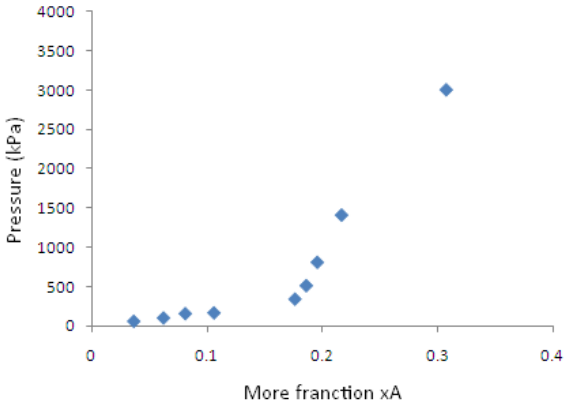


（a=1.95, k_A=0.04, b=1.2, k_B=35, m=1, n=2, k_{AB}=1.5）

Fig. 7. The impact of k_{AB} on CO_2 absorption by hexane(25℃)



(a=1.95, k_A=0.04, b=1.2, k_B=35, m=1, n=2, k_{AB}=5)



(a=1.95, k_A=0.04, b=1.2, k_B=35, m=1, n=2, k_{AB}=15)

Fig. 8. The impact of k_{AB}'s substantial increase on CO_2 absorption (25℃)

Because k_{AB} is relatively small, HE-IMC of hexane and CO_2 has little effect on VLE. Thus, changes of *m* and *n* have little or even no effect on VLE within quite a wide range.

When k_{AB} is small, just as CO_2 absorption by alkanes, it could be considered as physical absorption. When k_{AB} increases to a certain extent, it is found that phase equilibrium curves appear characteristics of chemical absorption, as shown in Fig. 8.

There still exists the possibility that IMC hypothesis expatiates on the mechanism of chemical absorption any further. It also indicates the orientation of further research in future.

V. Conclusion

Based on IMC hypothesis, this paper expatiates on the molecular interaction mechanism of CO_2 absorption by alkanes and fits parameters in IMC hypothesis. Fitting data agree well with experimental values (cited data).

Based on IMC Hypothesis, the impact of homogenous instantaneous molecule cluster among the alkane molecules on VLE is stronger than that of heterogeneous molecule cluster between CO_2 and solvent molecules, and that of homogenous instantaneous molecule cluster among CO_2 molecules. As carbon chain of absorbent elongation, formation probability and stability of the instantaneous molecule cluster decreases and absorption capacity increases. Based on IMC hypothesis, this paper expatiates on the molecular interaction mechanism of CO_2 absorption by

alkanes and fits parameters in IMC hypothesis. Fitting data agree well with experimental values (cited data).

According to the fitting results of CO_2 absorption by alkanes based on IMC hypothesis, linear correlation coefficients of the predicted values and the experimental values (cited data) can be larger than 0.99, when k_A, a, k_B, b, and k_{AB} take values within limits. Take hexane as an example, the best value ranges of k_A, a, k_B, b, and k_{AB} are 0.02-0.06, 1.8-2.2, 20-50, 1-1.3, 0-0.9, respectively.

IMC hypothesis, in principle, can be applied to physical absorption and chemical absorption. It is important to do further studies on other physical absorbents, such as alcohol, ketone and ethers, and chemical absorbent, such as ethanolamine.

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