

Modified van der Waals Equation for the Prediction of Multicomponent Isotherms



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A modified two-dimensional van der Waals equation model was proposed for the prediction of multicomponent gas–solid adsorption isotherms from corresponding single-component adsorption equilibrium data. The model was used to predict adsorption isotherms of CO–CO₂ mixtures and CO₂–N₂ mixtures on Cu(I)–NaY zeolite. Experimental adsorption equilibrium data of the two systems were compared with results calculated from the model and three other models in the literature: the ideal adsorbed solution model, the vacancy solution theory of adsorption using the Flory–Huggins activity coefficient equation, and the two-dimensional van der Waals equation. The results indicated that the modified van der Waals equation predicted the experimental results better than the three other models for the two systems studied, especially for the CO–CO₂ system, which involved chemical reaction during adsorption and exhibited azeotropic behavior. © 1998 Academic Press

Key Words: gas adsorption; isotherm; zeolite; equation of state.

INTRODUCTION

Mathematical modeling of multicomponent gas adsorption has undergone several changes in the past 40 years. Early in 1953, der Boer (1) provided several relationships between a two-dimensional equation of state and other physical models and explained the physical significance of the parameters of the equations of state. Hoory and Prausnitz (2) obtained an isotherm equation which can be used to predict binary mixture adsorption equilibria by combining the van der Waals equation and the exact thermodynamic relations. Payne *et al.* (3) used a two-dimensional equation of state derived from the Hirschfelder–Eyring modification of the van der Waals equation to predict the high-pressure adsorption of pure and mixed hydrocarbons on charcoal. Van Ness (4) thoroughly explained the concept of the two-dimensional phase and provided an accurate thermodynamic analysis for the two-dimensional van der Waals isotherm equation proposed by Hoory and Prausnitz (2). Patrykiewicz and co-workers (5) applied the generalized van der Waals theory for dense fluids to the physical adsorption of pure gases on homogeneous solid surfaces. They subsequently de-

rived a two-dimensional Peng–Robinson equation of state. Konno *et al.* (6) obtained a binary adsorption isotherm equation by modifying the two-dimensional Peng–Robinson equation of state.

Although many studies on the applications of thermodynamic equations of state in gas–solid adsorption equilibria have been carried out, they are still far behind those in gas–liquid equilibria. Based on the success of equations of state in gas–liquid equilibria, it is reasonable to expect that good results for the prediction of gas–solid equilibria may be achieved analogously. In this work, the two-dimensional van der Waals equation was modified by introducing a parameter *m* to predict adsorption isotherms of gas mixtures. The model parameters were derived from corresponding single-component gas adsorption equilibrium data. The accuracy of the model was demonstrated by comparing model calculations with experimental adsorption equilibrium data of CO–CO₂ mixtures and CO₂–N₂ mixtures on Cu(I)–NaY zeolite. Three other existing models in the literature were used for comparisons.

A MODIFIED TWO-DIMENSIONAL VAN DER WAALS EQUATION OF STATE

The study of gas–liquid equilibria plays an important role in solution thermodynamics. It gives a strong analogy for the study of gas–solid adsorption equilibria. There are substantial differences, but the essential similarity still exists. The gas phase does not extend unchanged all the way to the solid surface. Near the solid surface, the gas-phase properties change, but they do not change abruptly. The gradients of change may be steep, but they are not mathematically infinite. Nobody seems to know precisely the extent of the interfacial region nor the exact distance into the gas phase that the solid makes its influence felt. According to Van Ness (4), one can transform the actual interfacial region into an imaginary mathematical surface in which one imagines that the properties of the gas phase remain unchanged until the gas phase reaches this surface, which is treated as a two-dimensional phase with its own thermodynamic properties.

The concept of the two-dimensional phase provides us with a precisely defined system to which we may apply the equa-

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tions of state. We can not only account for the changes of properties of the gas phase in the interfacial region by means of the two-dimensional phase but also derive these changes from the three-dimensional gas phase. Several two-dimensional equations have been proposed for pure compounds. One that has received particular attention is the two-dimensional van der Waals equation by Hoory and Prausnitz (2),

$$\pi = \frac{KT}{\sigma - \beta} - \frac{\alpha}{\sigma^2}, \quad [1]$$

where π is the spreading pressure and K is Boltzmann's constant. α and β are two characteristic constants, and T is the absolute temperature. σ is defined as (2)

$$\sigma = \frac{A}{Nn^a}, \quad [2]$$

in which A is the surface area per unit weight of adsorbent available for adsorption, N is Avogadro's number, and n^a is the number of moles of adsorbed gas per unit weight of adsorbent. σ is the surface area allocated to each molecule when there is a monolayer coverage of the adsorption surface.

The modified van der Waals equation used in this work is obtained by introducing a parameter m into Eq. [1],

$$\pi = \frac{KT}{\sigma - \beta} \left(1 + m \frac{\beta}{\sigma} \right) - \frac{\alpha}{\sigma^2}. \quad [3]$$

This is the same two-dimensional van der Waals equation used by Hoory and Prausnitz (2) and Ruthven (7) except the addition of the m term. The significance of the parameter m will be discussed later.

Combining Eq. [3], the Gibbs equation (7)

$$\left(\frac{\partial P}{\partial \pi} \right)_T = \frac{AP}{n^a RT}, \quad [4]$$

and the mathematical relationship

$$\left(\frac{\partial \pi}{\partial A} \right)_T = \left(\frac{\partial \pi}{\partial \sigma} \right)_T \left(\frac{\partial \sigma}{\partial A} \right)_T, \quad [5]$$

the following pure-component adsorption isotherm can be obtained:

$$P = \frac{k' \theta}{(1 - \theta)^{m+1}} \exp \left[\frac{(m+1)\theta}{1 - \theta} - \frac{2\alpha\theta}{KT\beta} \right], \quad [6]$$

where P is the equilibrium pressure, θ is the fraction of surface area covered by adsorbed gas molecules, and $\theta = \beta/\sigma$ as

pointed out by Ruthven (7). The Henry's law constant k' in the equation is defined by

$$k' = \lim_{\theta \rightarrow 0} \frac{P}{\theta}. \quad [7]$$

Equation [6] reduces to the standard van der Waals isotherm presented by Ruthven (7).

For multicomponent mixed-gas adsorptions, σ is defined as

$$\sigma = \frac{A}{Nn_T^a}, \quad [8]$$

where n_T^a is the total adsorption amount. The constant β can be obtained from the equation

$$\beta = \frac{A}{Nn_i^\infty}, \quad [9]$$

in which n_i^∞ is the adsorption saturation amount of component i .

For a binary gas mixture, the following simple mixing rules are used:

$$\alpha_{12} = (\alpha_1 + \alpha_2)/2 \quad [10]$$

$$\alpha_m = x_1^2 \alpha_1 + 2x_1 x_2 \alpha_{12} + x_2^2 \alpha_2 \quad [11]$$

$$\beta_m = x_1 \beta_1 + x_2 \beta_2 \quad [12]$$

$$m = m_1 x_1 + m_2 x_2. \quad [13]$$

The surface fugacity of component 1 in the adsorbed mixture can be calculated from the thermodynamic relation (2)

$$RT \ln f_1^a = \int_A^\infty \left[\left(\frac{\partial \pi}{\partial n_1^a} \right)_{T, A, n_2^a} - \frac{RT}{A} \right] dA - RT \ln \frac{A}{n_1^a RT}, \quad [14]$$

where the definition of the surface fugacity is

$$d\mu_1^a = RT d \ln f_1^a \quad [15]$$

and

$$\lim_{\pi \rightarrow 0} \frac{f_1^a}{x_1 \pi} = 1, \quad [16]$$

in which μ_1^a is the chemical potential of component 1 in the adsorbed phase and x_1 is the mole fraction of component 1 in the adsorbed phase. In the gas phase, component 1 is consid-

ered as an ideal gas that observes the following relationship (2):

$$f_1^a = \frac{RT}{Nk'\beta_1} f_1^g = \frac{RT}{Nk'\beta_1} P y_1, \quad [17]$$

where P_t is the total equilibrium gas pressure and y_1 is the mole fraction of component 1 in the gas phase at equilibrium. Similar equations can be written for component 2. Integration of Eq. [14] yields the expression $\ln f_1^a$. Combining $\ln f_1^a$ with Eq. [17], we can obtain the isotherm equation for component 1 in a binary gas mixture as follows:

$$P_t y_1 = \frac{x_1 k'_1 \beta_1}{\sigma - \beta_m} \exp \left[\frac{m(3\beta_1 - 2\beta_m) + \beta_1}{\sigma - \beta_m} + \frac{m(2\beta_1 - \beta_m)}{\beta_m} \right. \\ \left. \times \ln \frac{\sigma}{\sigma - \beta_m} - \frac{2}{KT\sigma} (\alpha_1 x_1 + \alpha_{12} x_2) \right]. \quad [18]$$

When $m = 0$, this equation reduces to the isotherm equation derived by Hoory and Prausnitz (2) using the standard van der Waals equation. By symmetry, we can write down the following equation for component 2 based on Eq. [18]:

$$P_t y_2 = \frac{x_2 k'_2 \beta_2}{\sigma - \beta_m} \exp \left[\frac{m(3\beta_2 - 2\beta_m) + \beta_2}{\sigma - \beta_m} + \frac{m(2\beta_2 - \beta_m)}{\beta_m} \right. \\ \left. \times \ln \frac{\sigma}{\sigma - \beta_m} - \frac{2}{KT\sigma} (\alpha_2 x_2 + \alpha_{12} x_1) \right]. \quad [19]$$

The isotherm equations described here for a binary system can be readily extended to gas mixtures with more than two components when appropriate mixing rules are used.

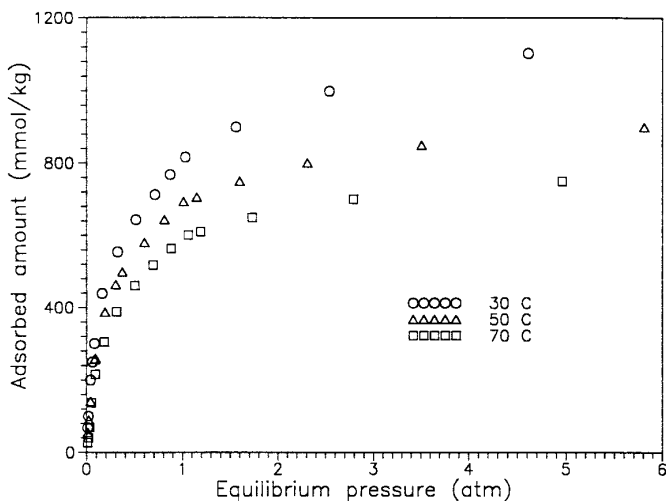


FIG. 1. Adsorption isotherms of CO on Cu(I)-NaY zeolite at three different temperatures.

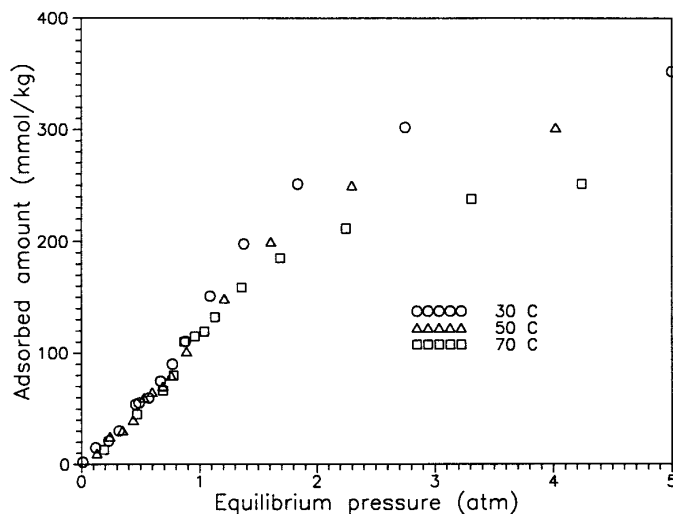


FIG. 2. Adsorption isotherms of CO₂ on Cu(I)-NaY zeolite at three different temperatures.

MATERIALS AND METHODS

NaY zeolite pellets (1 mm in diameter) were first pretreated with 1 N NaNO₃ solution and then with 0.1 N Cu(NO₃)₂ solution for ion exchange at room temperature. The resulting Cu(II)-NaY zeolite was light blue. It was washed with distilled water and dried at 110°C. Atomic absorption spectrometry of the zeolite indicated that the cupric content was 5.037% by weight.

The Cu(II)-NaY zeolite can be easily reduced to Cu(I)-NaY zeolite by reacting with hydrogen or carbon monoxide (8). In this work, carbon monoxide was used as the reduction agent. The Cu(II)-NaY zeolite was first dehydrated at 150°C and 10⁻⁶ mmHg (1.3 mPa), and then carbon monoxide was introduced to reduce the Cu(II) to Cu(I) at 250°C for 4 h. The final Cu(I)-NaY zeolite was gray white.

Adsorption isotherms of CO, CO₂, N₂, and their mixtures on Cu(I)-NaY zeolite were measured by the static volumetric method following Wilson and Danner (9). For the binary mixture isotherms, samples of the gas phase at adsorption equilibrium were analyzed using gas chromatography.

RESULTS AND DISCUSSION

1. Physical Adsorption of Gas Mixture

Four models were used to predict experimental mixed-gas adsorption equilibria. They were the ideal adsorbed solution model (IASM) of Myers and Prausnitz (10), Cochran *et al.*'s (11) vacancy solution theory of adsorption using the Flory-Huggins activity coefficient equation (F-H VST), the two-dimensional van der Waals equation (VAW) of Hoory and Prausnitz (2), and the modified van der Waals equation (this work). All four models used only the data obtained from

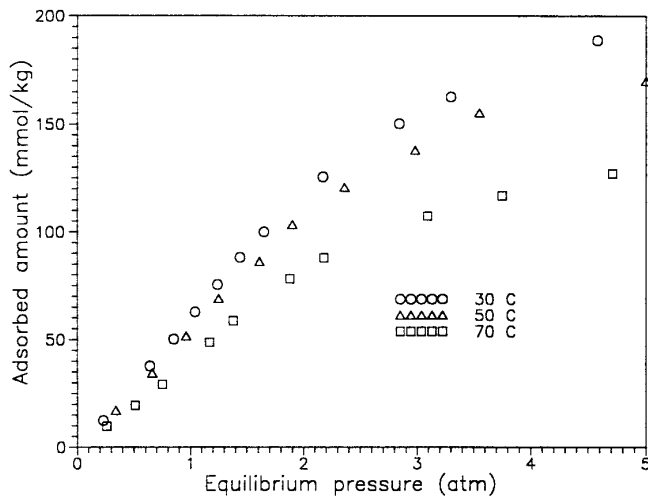


FIG. 3. Adsorption isotherms of N_2 on Cu(I)-NaY zeolite at three different temperatures.

single-component adsorption isotherms to predict the adsorption isotherm for the two binary gas systems.

The experimental adsorption isotherm data of pure components CO, CO_2 , and N_2 on Cu(I)-NaY zeolite are shown in Figs. 1–3. Parameters used in the models (see Table 1) were determined by correlating the isotherm data of the pure components. The good agreement between the experimental data and the model calculation indicates that the models are capable of describing adsorption equilibria of pure components CO, CO_2 , and N_2 on Cu(I)-NaY zeolite.

Figures 4–6 give the y - x diagrams (mole fraction in the gas phase vs mole fraction in the adsorbed phase) of the adsorption of CO_2 - N_2 mixtures on Cu(I)-NaY zeolite at three different

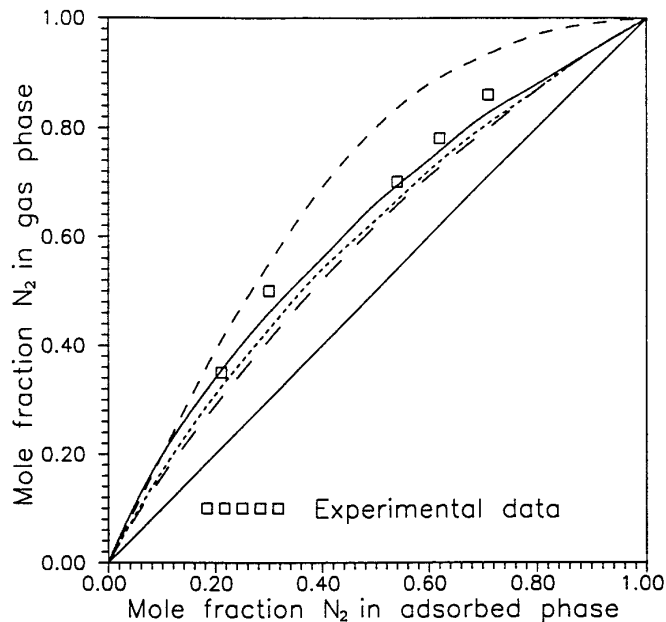


FIG. 4. Adsorption phase diagram for CO_2 - N_2 mixtures on Cu(I)-NaY zeolite at 30°C and 1 atm [(\cdots) IASM; ($---$) F-H VST; ($- \cdot -$) VAW; ($---$) this work].

temperatures and 1.0 atm. For this physical adsorption system, results predicted by these four models using the parameters listed in Table 1 are all in good agreement with the experimental data. The largest relative error is less than 12%. The results also demonstrate that although the ideal adsorbed solution model has the simplest form, it gives good predictions comparable to those from other relatively more complex models. The same conclusion was reached by Wilson and Danner (9).

TABLE 1
Model Parameters Correlated from the Isotherm Data of Pure Gases on Cu(I)-NaY Zeolite

T (°C)	van der Waals equation		This work ^a			F-H VST ^b		
	$\ln k'$	$-2\alpha/KT\beta$	m	$\ln k'$	$-2\alpha/KT\beta$	n_i^∞	b_i	α_{1v}
CO								
30	-0.87837	-3.08813	-0.90345	-1.83461	3.34024	1.30115	90.5811	5.00749
50	-1.17653	-0.96900	-0.48038	-1.46688	1.62495	1.19733	3.98263	-0.89621
70	-0.98027	-0.60831	-0.00342	-0.98102	-0.59744	1.08655	3.72785	-0.97809
CO_2								
30	1.95741	-3.54817	0.85726	2.04508	-6.43355	0.65828	0.21404	0.81826
50	1.97888	-3.43705	0.89711	2.05952	-6.30123	0.62382	0.34752	0.42381
70	1.80964	-2.88271	0.82026	1.91423	-5.50739	0.55187	0.19921	-0.84614
N_2								
30	2.11830	-2.14888	0.40374	2.14860	-3.31240	0.49800	0.08181	-0.59544
50	2.10870	-1.99856	0.49923	2.14747	-3.44641	0.45328	0.08804	1.23839
70	2.30022	-1.72860	0.40572	2.31705	-2.80203	0.41034	0.06195	1.35422

^a Modified van der Waals equation.

^b Vacancy solution theory of adsorption using the Flory-Huggins activity coefficient equation.

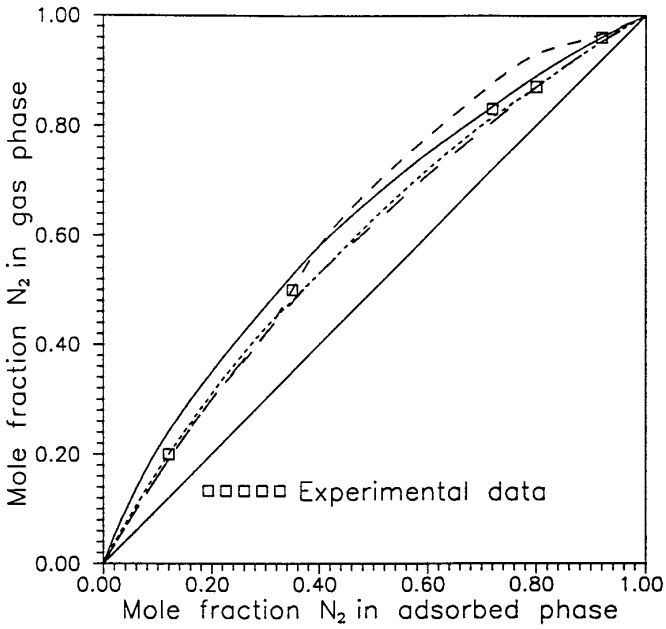


FIG. 5. Adsorption phase diagram for CO₂-N₂ mixtures on Cu(I)-NaY zeolite at 50°C and 1 atm [(· · ·) IASM; (---) F-H VST; (- - -) VAW; (—) this work].

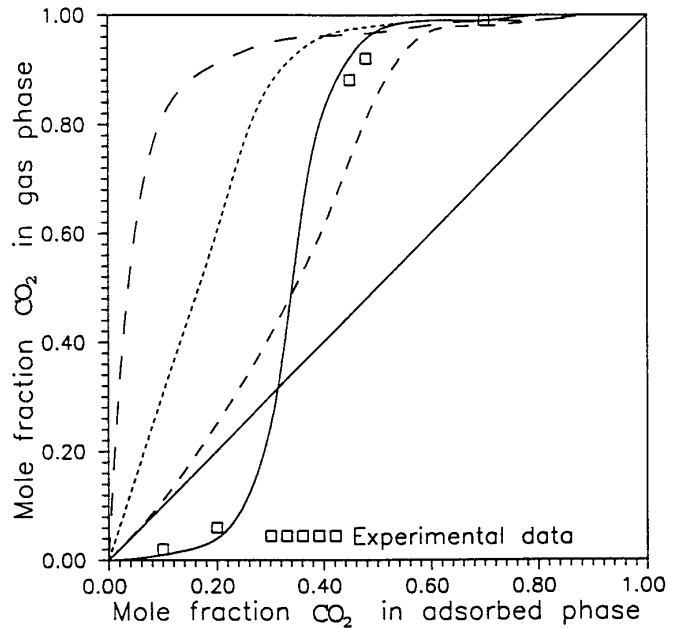


FIG. 7. Adsorption phase diagram for CO-CO₂ mixtures on Cu(I)-NaY zeolite at 30°C and 1 atm [(· · ·) IASM; (---) F-H VST; (- - -) VAW; (—) this work].

2. Simultaneous Physical and Chemical Adsorption of Gas Mixtures

The adsorption of CO-CO₂ mixtures on Cu(I)-NaY zeolite is a special system in which physical adsorption and chemical adsorption occur simultaneously. A chemical reaction between

the ion Cu(I) and carbon monoxide takes place (8) while the physical adsorption of carbon dioxide on the adsorbent occurs. The experimental equilibrium data shown in Figs. 7-9 indicate that there exists an azeotropic point when the mole fraction of carbon dioxide in the adsorbed phase x is in the range of 0-0.3.

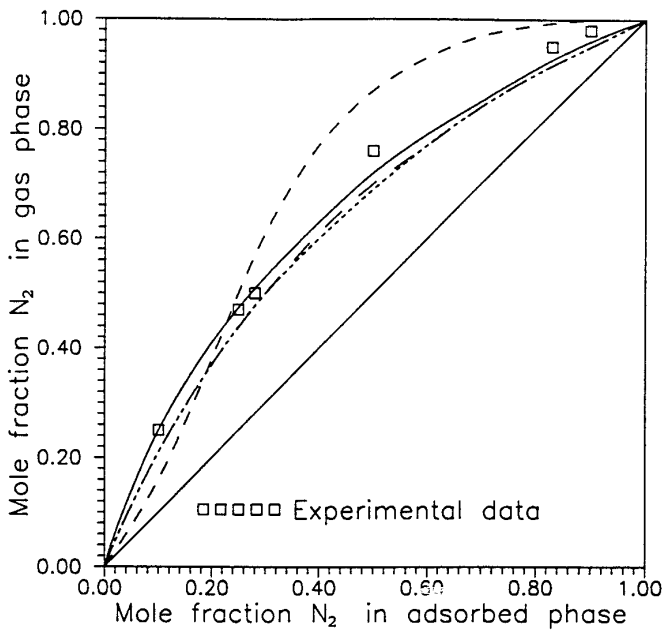


FIG. 6. Adsorption phase diagram for CO₂-N₂ mixtures on Cu(I)-NaY zeolite at 70°C and 1 atm [(· · ·) IASM; (---) F-H VST; (- - -) VAW; (—) this work].

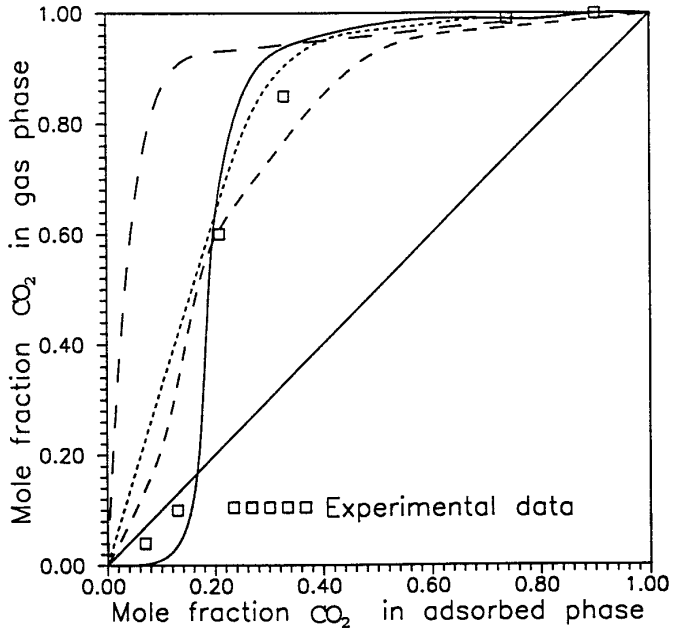


FIG. 8. Adsorption phase diagram for CO-CO₂ mixtures on Cu(I)-NaY zeolite at 50°C and 1 atm [(· · ·) IASM; (---) F-H VST; (- - -) VAW; (—) this work].

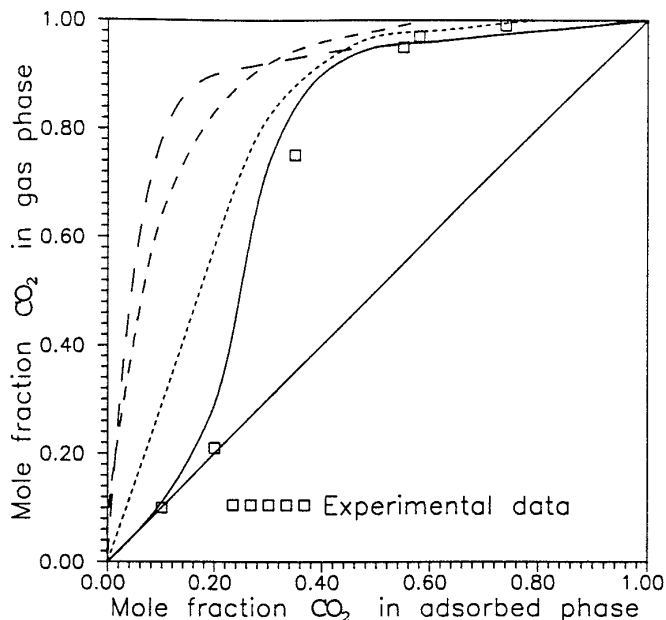


FIG. 9. Adsorption phase diagram for CO-CO₂ mixtures on Cu(I)-NaY zeolite at 70°C and 1 atm [(· · ·) IASM; (---) F-H VST; (- · - ·) VAW; (—) this work].

This azeotropic point disappears gradually with increasing temperature. Thus a higher temperature is preferred when one separates CO from the CO-CO₂ mixture using Cu(I)-NaY zeolite in order to avoid the azeotropic point.

Azeotropy in adsorption processes using zeolite, although not a common phenomenon, has been reported before. Hyun and Danner (12) studied azeotropic adsorption of C₂H₄-CO₂, *i*-C₄H₁₀-C₂H₄, *i*-C₄H₁₀-C₂H₆, and *i*-C₄H₁₀-C₂H₆ mixtures on 13X zeolite. It is interesting to note that the isotherms of *i*-C₄H₁₀ on 13X zeolite are similar to those of CO on Cu(I)-NaY zeolite. Both of them are very favorable isotherms. The difference is that the former involves only physical adsorption, while the latter involves chemical adsorption. According to Hyun and Danner (12), the vacancy solution theory of adsorption can be used to predict azeotropic adsorption quantitatively, but the ideal adsorbed solution model fails to predict any azeotropic points. However, for azeotropic adsorption of CO-CO₂ mixtures on Cu(I)-NaY zeolite, the vacancy solution theory of adsorption using the Flory-Huggins activity coefficient equation is not effective. Figures 7-9 show that all four models, except the modified two-dimensional van der Waals model, failed to predict the azeotropic point. The introduction of the parameter m in the modified two-dimensional van der Waals equation is the key to its successful prediction of the azeotropic point in the adsorption of CO-CO₂ mixtures on Cu(I)-NaY zeolite.

3. Significance of Parameter m

Values of m in Table 1 show that they are all positive for physical adsorption of either CO₂ or N₂ on Cu(I)-NaY zeolite

and negative for chemical adsorption of CO on Cu(I)-NaY zeolite. The first term on the right-hand side of Eq. [3] is the repulsive force term and the second the attractive force term. A negative value of m means that the attractive force increases while the repulsive force decreases relatively due to chemical reaction between CO and ion Cu(I). An increased value of m indicates the repulsive force increases but the attractive force decreases with increasing temperature. In this work, the introduction of m in Eq. [3] can be regarded as a modification of the repulsive force term.

The m value for Fig. 9 is very close to zero (see Table 1), unlike those for Figs. 7 and 8. This is because Fig. 9 does not show a clear-cut azeotropic point whereas Figs. 7 and 8 do. When $m = 0$, the modified two-dimensional van der Waals equation reduces to the regular two-dimensional van der Waals equation. However, in physical adsorption situations, the addition of m still can serve the purpose of improving the prediction accuracy as indicated in Figs. 4-6.

SUMMARY

The predictions from the four models—the adsorbed ideal solution theory, the vacancy solution theory of adsorption using the Flory-Huggins activity coefficient equation, the two-dimensional van der Waals equation, and the model of this work (the modified two-dimensional van der Waals equation)—were all in quantitative agreement with the experimental adsorption equilibrium data for CO₂-N₂ mixtures on Cu(I)-NaY zeolite.

For the adsorption of CO-CO₂ mixture on Cu(I)-NaY zeolite, in which the physical adsorption between CO₂ and the adsorbent and the chemical adsorption of CO on the ion Cu(I) occurred simultaneously, only the modified two-dimensional van der Waals equation was in good agreement with the experimental data. This semiempirical model also predicted the azeotropic point in this adsorption system. It is a useful addition to the family of equations of state which have important uses in process design.

Nomenclature

A	Area of adsorbent available for adsorption (m ² /kg)
b_1	Parameter in the vacancy model
f^a	Surface fugacity (atm)
f^g	Gas fugacity (atm)
K	Boltzmann constant
k'	Henry's constant (atm)
m	Parameter of the modified van der Waals equation
N	Avogadro's number
n_i^a	Adsorbed amount of component i (mol/kg)
n_T^a	Total adsorption amount (mol/kg)
P	Equilibrium pressure for pure gas system (atm)
P_t	Total equilibrium pressure for gas mixture (atm)
R	Gas constant

T	Absolute temperature (K)
x	Mole fraction in the adsorbed phase
y	Mole fraction in the gas phase

μ	Chemical potential
π	Spreading pressure (atm)
σ	Area allocated to each molecule defined in Eq. [2] (larger than actual molecular area) (m ²)

Subscripts

i	Component i
m	Mixture

Superscripts

a	Adsorption
∞	Saturation amount

Greek letters

α	Parameter in the van der Waals equation
α_{1v}	Parameter in the vacancy model
β	Actual area of each molecule at monolayer coverage
θ	Fraction of surface area covered by adsorbed gas molecules

REFERENCES

1. der Boer, J. H., "The Dynamical Character of Adsorption." Clarendon Press, Oxford, 1953.
2. Hoory, S. E., and Prausnitz, J. M., *Chem. Eng. Sci.* **22**, 1025 (1967).
3. Payne, H. K., Sturolevant, G. A., and Leland, A., *Ind. Eng. Chem. Fundam.* **7**, 363 (1968).
4. Van Ness, H. C., *Ind. Eng. Chem. Fundam.* **8**, 464 (1969).
5. Patrykiewicz, A., Jaroniec, M., and Rudzinski, W., *Chem. Eng. J.* **15**, 147 (1978).
6. Konno, M., Terabayashi, M., and Takako, Y., *J. Chem. Eng. Jpn.* **18**, 398 (1985).
7. Ruthven, D. M., in "Principles of Adsorption and Adsorption Processes," pp. 67, 69. John Wiley, New York, 1984.
8. Huang, Y. Y., *J. Catal.* **30**, 187 (1973).
9. Wilson, R. J., and Danner, R. P., *J. Chem. Eng. Data* **28**, 14 (1983).
10. Myers, A. L., and Prausnitz, J. M., *AIChE J.* **11**, 121 (1965).
11. Cochran, T. W., Kabel, R. L., and Danner, R. P., *AIChE J.* **31**, 268 (1985).
12. Hyun, S. H., and Danner, R. P., *J. Chem. Eng. Data* **27**, 196 (1982).