

ADSORPTION EQUILIBRIA FOR HYDROGEN AND CARBON DIOXIDE ON ACTIVATED CARBON AT HIGH PRESSURE UP TO 30 ATM

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Abstract—Equilibrium data for the adsorption of hydrogen, carbon dioxide, and binary mixture of both gases on activated carbon were determined experimentally. Pure component isotherms were presented along with pressures up to 30 atm at 301 K, 323 K and 348 K. Also, the binary equilibria were obtained at various temperatures same above for pressure of 1.5, 10 and 20 atm, respectively. For the pure component system, Freundlich isotherm was shown to be fitted best to the experimental results. However, in the binary system, the ideal adsorption solution (IAS) theory gave good representation of the binary experimental data in high pressure range.

INTRODUCTION

In the design and optimization of adsorption separation processes basic experimental equilibrium data at wide ranges of temperature and pressures are required. An abundance of pure gas equilibrium data at low pressure ranges exist in the literature, however available experimental data at high pressures are very limited. Moreover, since the adsorption separation processes involve the adsorption of multicomponent mixtures, multicomponent equilibria are required.

A number of models to predict the adsorption equilibria have been proposed by many investigators. Some models for the pure component system were summarized in Table 1. For over 60 years, the Langmuir or the Freundlich equation has been used to predict adsorption equilibrium data. The Langmuir equation [1] has theoretical background but this does not predict experimental data accurately where adsorbent surfaces are heterogeneous with respect to the energy of adsorption. On the other hand, Freundlich equation was known to be suitable for energetically heterogeneous surfaces, but this cannot be reduced to Henry's law if concentration approaches to zero. To overcome the deficiencies for these two isotherms, Redlich and Peterson [2] proposed an empirical equation which is combined Langmuir equation with Freundlich one. Also Radke and Prausnitz [3] propos-

ed similar equation.

Toth [4] suggested a new type of equation to investigate the adsorption of gases onto heterogeneous surface. Koresh and Soffer [6] modified the Langmuir model in order to cope with the two limitations: the surface homogeneity and monolayer adsorption. They proposed independent two-site Langmuir model and superimposed two-site Langmuir model. In the latter model, they assumed that the adsorption at the second site is not independent but associated with the molecules already adsorbed at the first site. Ruthven et al. [8] derived an isotherm for the adsorption on zeolites which was based on statistical thermodynamics, and extended later for the prediction of binary adsorption equilibria [11]. In this model, it is assumed that the adsorbate molecule is confined to a particular cavity but not adsorbed at specific localized site within the cavity.

The isotherms to predict multicomponent system can be divided into the two groups as shown in Table 2. The parameters in group I contains those of single component system. But for the second group models, multicomponent data are required to obtain the isotherm parameters. The first group models have an advantage that pure component experimental data are only required, but they do not predict the experimental data well over the entire concentration range. However, the second group models have good agreements with the experimental data over the entire concentration range better than those of the first group models

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Table 1. Isotherms for single component

Type	Relationship	Parameters	Characteristics
Langmuir [1]	$q = \frac{a p}{1 + b p}$	a, b	Homogeneous monolayer
Freundlich	$q = k p^{1/n}$	k, n	Heterogeneous not reduce to Henry's law
Redlich and Peterson [2]	$q = \frac{a p}{1 + b p^m}$	a, b, m	Combined Langmuir and Freundlich
Langmuir-Freundlich [7]	$q = \frac{a p^{1/n}}{1 + b p^{1/n}}$	a, b, n	Hybrid Langmuir and Freundlich
Generalized Toth [4]	$q = \frac{a(p/b)^m}{1 + (p/b)^m - (p/b)^n}$	a, b, m, n	Heterogeneous multilayer
Two-site Langmuir model [6]	$q = \frac{a_1 p}{1 + b_1 p} + \frac{a_2 p}{1 + b_2 p}$	a ₁ , b ₁	Independent two-site
	$q = \frac{a_1 p}{1 + b_1 p} \left(1 + \frac{a_2 p}{1 + b_2 p}\right)$	a ₂ , b ₂	Superimposed two site
Statistical model [8]	$q = \frac{kp + (kp)^2 \Gamma_n}{1 + kp + (kp)^2 \Gamma_n / 2}$	k, Γ _n	Two adsorbate molecules

Table 2. Isotherms for multicomponent

Groups	Investigators	Type
I, II	Butler and Ockrent [9]	$q = \frac{a_i p_i}{1 + \sum b_i p_i}$ j=1, N
	Yon and Turnock [10]	$q = \frac{a_i p_i^{1/n}}{1 + \sum b_i p_i^{1/n}}$ j=1, N
I	Ruthven and Wong [11]	$q = \frac{k_i p_i (1 + \sum k_j p_j \Gamma_{j,i})}{1 + \sum k_i p_i (1 + \sum k_j p_j \Gamma_{j,i})}$ j, k=1, N
	Redlich and Peterson [2]	$q = \frac{a_i p_i}{1 + \sum b_i p_i}$ j=1, N
	Mayer and Prausnitz [12] Suwanayuen and Danner [13]	Ideal Solution Theory Iterative Method Vacancy Solution Theory Iterative Method
II	Sheindorf et al. [14]	$q = a_i p_i (w_i p_i)^{m_i - 1}$ j=1, N
	Fritz and Schlunder [15]	$q = \frac{a_i p_i^m}{b_i + \sum a_j p_j^m}$ j=1, N

I: First group, II: Second group

since they use a multicomponent experimental data.

Extended Langmuir equation for the adsorption of mixed gas is a direct extension of the pure component Langmuir isotherm. Like the extended Langmuir model for mixture, the Langmuir-Freundlich isotherm for the pure component system can be extended to the multicomponent system. This is the LRC (Loading Ratio Correlation) equations in the multicomponent system. Both the extended Langmuir equation and the LRC equations lack a rigorous theoretical foundation. Because of their mathematical simplicity, however, the extended Langmuir and LRC equations have been predominantly used in the modeling and design of adsorbers and cyclic gas separation process for concen-

trated mixtures.

The ideal adsorbed solution (IAS) model of Mayers and Prausnitz [12] is based on solution thermodynamic concepts, but it is assumed that the adsorbed solution is ideal, and all activity coefficients set to unity. Suwanayuen and Danner [13] developed an isotherm model based on treating the adsorption equilibrium as an osmotic equilibrium between two vacancy solutions having different compositions. One solution represented the gas phase and the other the adsorbed phase. Both vacancies were hypothetical entity representing volume voids in the vapor phase or in the adsorbed phase which could be occupied by the adsorbate molecule that is the vacancy solution is composed

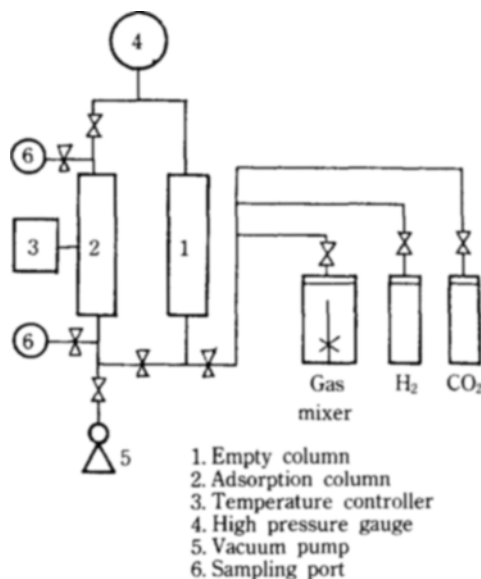


Fig. 1. Apparatus for adsorption isotherm experiment.

of adsorbate and vacancies. Equation of state was derived for the model by applying thermodynamic equations governing the equilibrium of the system. For the non-ideality of the adsorbed phase, activity coefficient was accounted whose composition dependence was described by Wilson equation.

The objectives of this study are to obtain the adsorption equilibrium data at high pressure and select one of the adsorption isotherm models that is fitting to the experimental data and to investigate the adsorption characteristics of hydrogen and carbon dioxide on activated carbon.

EXPERIMENTALS

A volumetric type apparatus was used to determine the equilibrium isotherms for the single and binary systems. The internal volume of the various parts of the system was accurately measured from expanding helium gas. A schematic diagram of the apparatus was shown in Fig. 1. It was composed of an adsorption vessel, a holding vessel, vacuum pump, high pressure gauge, temperature controller and gas cylinders. Pressure of the gas phase was measured by Heise high pressure gauge with high accuracy. The adsorption and holding vessels were made of stainless steel and kept a desired constant temperature of adsorption using a temperature controller in an accuracy of ± 0.5 K. The dead volume of the adsorption and holding vessel were 8.0 and 88.4 cm³, respectively. In the binary experiments, the gas phase compositions were

Table 3. Operating conditions of GC for concentration analysis

Packing materials	Activated charcoal (40/80 mesh)
Column length	40 cm
Carrier gas	Nitrogen
Column temperature	353 K
Injection temperature	373 K
Detector temperature	373 K
Detector	TCD

Table 4. Properties of activated carbon adsorbent

BET surface area (m ² /g)	477.88
Apparent density (g/cm ³)	0.684
True density (g/cm ³)	2.521
Pore volume (cm ³ /g)	1.065

analyzed by a gas chromatography and the operating conditions of GC for concentration analysis are given in Table 3.

The adsorbent used in experiments was an activated carbon, supplied by Aldrich Chemicals Ltd. of 20-40 mesh size and its physical properties are given in Table 4. The purity of carbon dioxide and hydrogen reported by the manufacturer are 99.5% minimum, respectively.

Pure component adsorption isotherms of carbon dioxide and hydrogen on activated carbon were measured at three temperatures; 301 K, 323 K, 348 K and pressures up to 30 atm. A static equilibrium technique was used for the measurement of the pure gas adsorption isotherms. A measured amount of gas was introduced to the adsorption cell containing the weighed adsorbent sample. The amount of gas adsorbed was hence determined by performing a material balance on the number of moles present in the gas and the adsorbed phase before and after the addition of a new dose of gas to the adsorption vessel using the appropriate P-V-T measurements. Correction for deviation from the ideal gas laws were made especially at high pressure, this could be carried out by using the virial equation of state. Details of the calculation procedures were given elsewhere [16].

RESULTS AND DISCUSSION

1. Single Component System

Adsorption isotherms of pure carbon dioxide and hydrogen gas were shown in Fig. 2 and Fig. 3, respectively, for each experimental temperature. These figures represent the behavior of adsorption equilibrium for each component, and the solid line in the figures re-

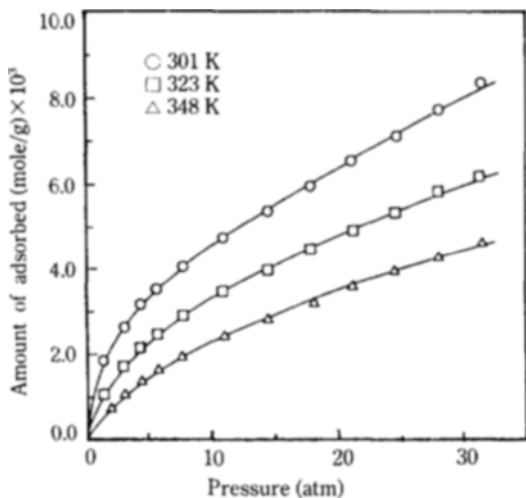


Fig. 2. Adsorption isotherm curves of CO₂ on activated carbon at 301 K, 323 K and 348 K.

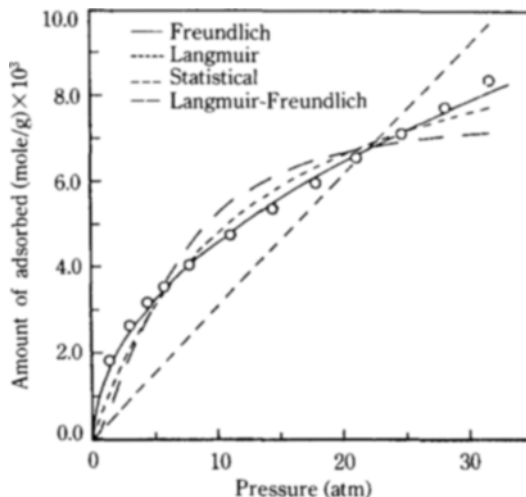


Fig. 4. Comparison of model with experimental data of CO₂ on activated carbon at 301 K.

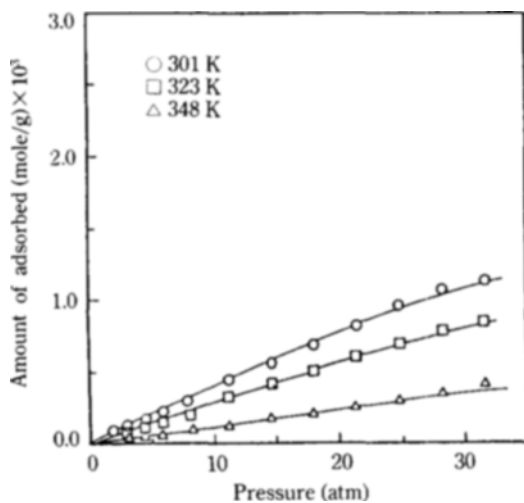


Fig. 3. Adsorption isotherm curves of H₂ on activated carbon at 301 K, 323 K and 348 K.

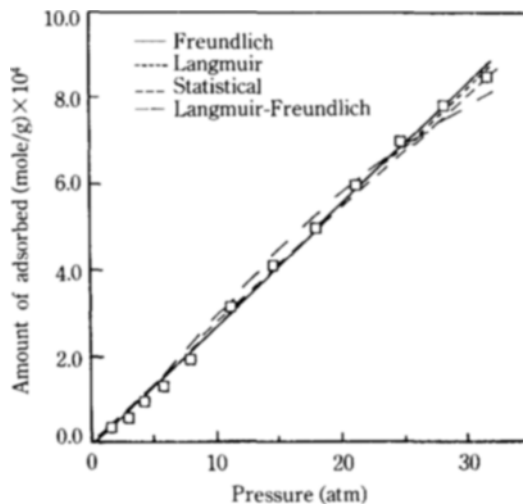


Fig. 5. Comparison of model with experimental data of H₂ on activated carbon at 323 K.

presents the connection of the experimental data point. As illustrated in Fig. 2 and Fig. 3, the amount of the pure gas adsorption of hydrogen was one order of magnitude lower than that of carbon dioxide in spite of the same temperature and pressure. Thus, we could expect that the separation of hydrogen from hydrogen-carbon dioxide gas mixture can be made easily by adsorptive gas separation processes.

It was frequently reported that a maximum appears on the isotherms of high pressure gas, and a reasonable explanation had already been given [17]. Ozawa et al. [18] examined the maximum phenomena of ad-

sorption for various gases on MS-5A adsorbent at pressure up to 100 atm. They found that, under their experimental conditions, amount of adsorption of argon and carbon monoxide were increased monotonously with equilibrium pressure, while the adsorption maxima were observed for carbon dioxide, methane, ethylene and ethane. According to the Ozawa's data, the equilibrium pressure of maximum adsorption for carbon dioxide on MS-5A adsorbent was about 40 atm at 348 K, and in the case of methane was 70 atm at the same temperature. However, the maximum did not appear in our experimental conditions for the acti-

Table 5. Parameter values of the Langmuir isotherm on activated carbon

Component	Temp.(K)	a	b	AD(%)
CO ₂	301	.1078E-01	.8054E-01	8.80
	323	.8826E-02	.6308E-01	7.43
	348	.9697E-02	.4364E-01	6.18
H ₂	301	.1597E-01	.2479E-02	3.94
	323	.9997E+00	.2741E-04	12.67
	348	.8000E+02	.1564E-06	14.11

*Average percent deviation was defined as

$$AD(\%) = \frac{1}{N_d} \sum_i |(q_{cal} - q_{exp})/q_{exp}| \times 100$$

ated carbon adsorbent. If the equilibrium pressure of adsorption had been increased further, a maximum point in the adsorption isotherm would be expected.

The experimental adsorption isotherm data of single component system were correlated with the Langmuir isotherm, Freundlich isotherm, Langmuir-Freundlich isotherm, and the statistical thermodynamic model. The isotherm equations mentioned above provide non-linear relationships between the two observable (P, q) for a given set of adjustable parameters. Estimates of these parameters are obtained by fitting the equation to N_d set of data. This was achieved by numerical minimization of the residual sum of squares computed by a numerical method based upon the powell's optimization algorithm. Namely, the least-squares criteria for extracting the constants of each equation from N_d data point were

$$\text{Minimize} \left(\sum_{i=1}^{N_d} [q_{i, cal} - q_{i, exp}]^2 \right)$$

Fig. 4 and Fig. 5 represent the comparison of the experimental results with the various models. As shown in these figures, the experimental results were best represented by the Freundlich isotherm for both cases of the carbon dioxide and hydrogen. The Langmuir and Langmuir-Freundlich isotherms were also agreed fairly well with the experimental results, but the statistical thermodynamic model showed the large deviations from the experimental results.

The parameter values obtained for the Langmuir and Freundlich isotherm was given in Table 5 and Table 6, respectively, and they exhibited a certain tendency. Kim et al. [19] reported that if the value of exponent parameter 1/n of the Freundlich isotherm became small the affinity of the component increased. Also, as the values of the Langmuir parameter b and the parameter k in the statistical model increased, it has been noticed that the physical meaning of the model is the same as that of the Freundlich isotherm.

Table 6. Parameter values of the Freundlich isotherm on activated carbon

Component	Temp.(K)	k	1/n	AD(%)
CO ₂	301	.1441E-02	.5011E+00	2.06
	323	.9187E-03	.5503E+00	1.67
	348	.5461E-03	.6185E+00	1.53
H ₂	301	.4074E-04	.9720E+00	4.28
	323	.2389E-04	.1043E+01	9.33
	348	.1784E-05	.1147E+01	8.28

*Average percent deviation was defined as

$$AD(\%) = \frac{1}{N_d} \sum_i |(q_{cal} - q_{exp})/q_{exp}| \times 100$$

That is, 1/n, b and k are constants related to the energy of adsorption. From Table 5 and Table 6, it could be seen that the affinity of carbon dioxide with respect to the surface of activated carbon was higher than those of hydrogen. Also, the temperature dependence of the parameters were summarized in Table 7. In Table 7, Henry's constant was assumed in the exponential temperature dependent form, and the other parameters were assumed as given in Table 7.

2. Binary System

Binary equilibrium data of carbon dioxide and hydrogen gas mixtures on activated carbon were determined on three temperatures; 301, 323, and 348 K, and at three pressures; 1.5, 10 and 20 atm. The adsorbed amount of each gas were determined by performing a component material balance on the number of moles present in the gas and adsorbed phase before and after the addition of a new dose of gas to the adsorption vessel. This was done using the P-V-T measurements and analysis by gas chromatography.

In order to completely specify the adsorption equilibria at a given temperature and total pressure when a binary gas mixture is adsorbed, the composition of the gaseous and the adsorbed phase must be specified together with the total amount adsorbed. The method of presentation of these variables is to plot the total amount adsorbed per unit mass of adsorbent as a function of the gas phase composition. The experimental results were shown typically in Fig. 6 and Fig. 7.

The models used in this study for the prediction of the binary adsorption equilibria were extended Langmuir model [9], LRC model [10], IAS theory [12], and simplified statistical thermodynamic model [11]. All of these models were used to predict binary adsorption equilibria by the pure component adsorption isotherm parameters. Comparison of theoretical prediction of various models with experimental data of carbon dioxide-hydrogen gas mixture on activated carbon at 301 K were shown in Fig. 8 and Fig. 9, by adsorp-

Table 7. Parameter values as the function of temperature (Temp. : K)

Langmuir parameters			
Component	a		b
CO ₂	.85588E + 04/T ^{2.3815}		.10585E - 02Exp (1308.0/T)
H ₂	.55323E + 05/T ^{2.2411}		.74426E - 06Exp (1917.7/T)
Freundlich parameters			
Component	k		1/n
CO ₂	.1321E - 05Exp (2107.6/T)		1.3673 - 261.93/T
H ₂	.9197E - 06Exp (1102.4/T)		3.3447 - 373.68/T
Langmuir-Freundlich parameters			
Component	a	b	1/n
CO ₂	1139.4/T ^{2.5042}	.9297E - 06Exp (3293.9/T)	.1997E + 01 - 140.9/T
H ₂	1156.1/T ^{2.3563}	.3573E - 02Exp (319.2/T)	.2187E + 01 - 137.9/T
Statistical model parameters			
Component	k		
CO ₂	.3342E - 05Exp (1363.4/T)		
H ₂	.8517E - 06Exp (1098.9/T)		

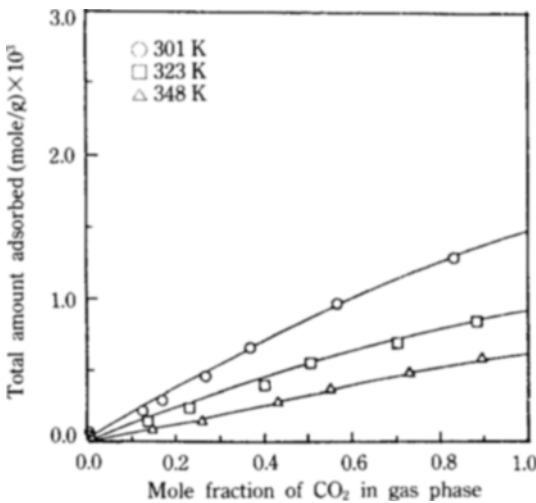


Fig. 6. Binary adsorption equilibria data of CO₂/H₂ on activated carbon at P=1.5 atm.

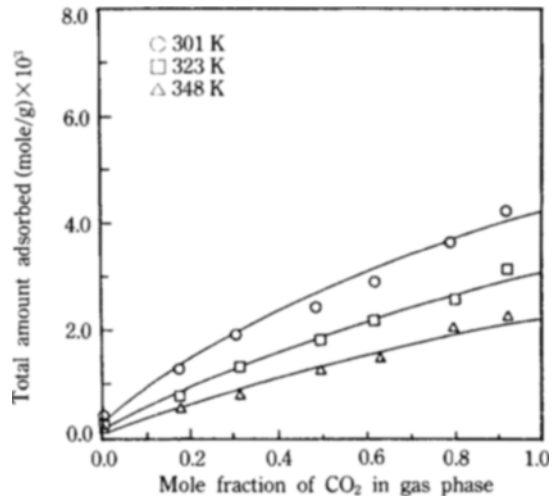


Fig. 7. Binary adsorption equilibria data of CO₂/H₂ on activated carbon at P=10 atm.

tion phase diagrams. The IAS theory gave the best representation of the binary experimental data when the total pressure was 1.5 atm in Fig. 8. However, in Fig. 9, when the total pressure was 10 atm, the LRC model had a good agreement with the experimental data. Similar results was obtained when the total pressure was 20 atm.

The IAS theory had a good agreement with the experimental data at the low pressure but large deviations appeared in the high pressure region. This is

quite obvious since the deviation from ideality was pronounced when the total pressure is very high. The simplified statistical thermodynamic model was derived specifically for an adsorption of zeolite, but we have tried to apply it to the activated carbon adsorbent system. However, the predictions for this simple statistical thermodynamic model were not as good as the other one.

Also, for the purpose of modeling and design of the packed column or of the separation process sys-

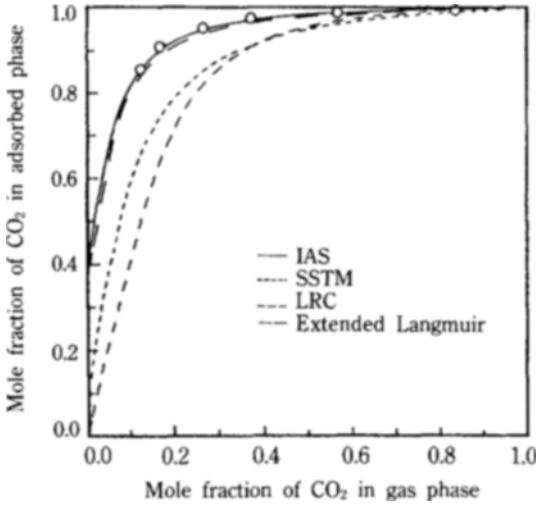


Fig. 8. Comparison of various models with experimental data of CO₂/H₂ on activated carbon at 301 K (P= 1.5 atm).

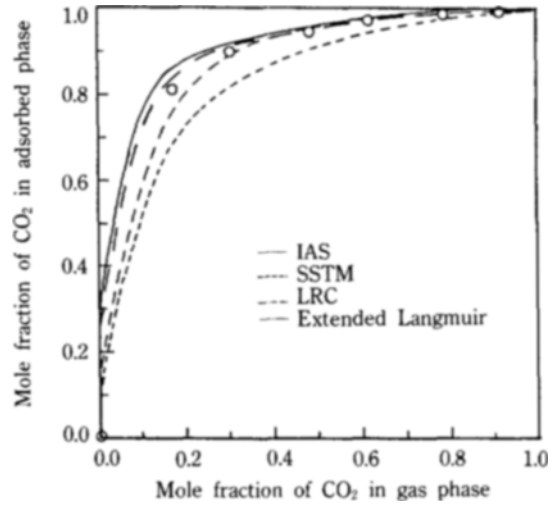


Fig. 9. Comparison of various models with experimental data of CO₂/H₂ on activated carbon at 301 K (P= 10 atm).

Table 8. Empirical correlation parameter values of the extended Langmuir model for activated carbon

Comp.	P(atm)	T(K)	a	b ₁	b ₂	AD(%)
CO ₂	1.5	301	.2552E-02	.9936E+00	.7696E+00	7.70
		323	.6878E-01	.1177E-01	.6450E-01	7.74
		348	.4967E+00	.1104E-02	.4517E+00	7.02
	10	301	.5665E-03	.6782E+00	.2814E+01	5.87
		323	.6249E-02	.1182E+00	.9853E-01	3.92
		348	.3849E-02	.1998E+00	.2533E+00	2.77
	20	301	.8290E-02	.1727E+00	.1168E+00	5.41
		323	.7186E-02	.9910E-01	.5616E-01	5.47
		348	.5521E-02	.9881E-01	.7010E-01	6.47
H ₂	1.5	301	.4896E-04	.4479E+00	.1424E+01	4.53
		323	.6546E-04	.5358E+00	.1906E+01	8.62
		348	.1113E-03	.2044E+00	.2988E+01	8.90
	10	301	.5480E-03	.2961E+00	.9389E+00	11.12
		323	.4560E-03	.6976E+00	.3461E+01	13.38
		348	.4231E-03	.7052E+00	.6134E+01	19.28
	20	301	.1346E-02	.2182E+00	.1417E+01	10.01
		323	.8048E-03	.4032E+00	.2709E+01	10.98
		348	.2955E-03	.7138E+00	.2344E+01	9.81

*Average percent deviation was defined as

$$AD(\%) = \frac{1}{N_d} \sum |(q_{cal} - q_{exp}) / q_{exp}| \times 100$$

tems, the extended Langmuir equation parameters were determined directly from the correlation of the binary experimental data. A nonlinear least-square method utilizing the Powell's optimization algorithm was used to obtain the extended Langmuir parameters from the binary adsorption data. The values of the extended Langmuir parameters calculated from the

binary experimental data and the average percent deviations were summarized in Table 8.

Because of using the binary experimental data, the empirical correlation of the extended Langmuir equation represented the binary equilibrium data more accurately than that of using pure component system parameters.

CONCLUSIONS

Adsorption equilibria for hydrogen, carbon dioxide and binary mixture of both gases on activated carbon were obtained at wide ranges of temperature and pressure. The experimental results for the pure component system were best represented by the Freundlich isotherm for hydrogen and carbon dioxide. The Langmuir and Langmuir-Freundlich isotherms were also agreed with the experimental results, while the statistical thermodynamic model showed large deviations from the experimental results. The parameters of each model for the single component system were represented as a function of temperature. For the binary system, the IAS model gave a good representation of the experimental results at low pressure ranges, and the LRC model gave the good representation of the experimental results at high pressure ranges.

NOMENCLATURE

a, a_i : parameters for adsorption isotherm
 b, b_i : parameters for adsorption isotherm
 k, k_i : parameters for adsorption isotherm
 m : parameter for adsorption isotherm
 N : numbers of component
 N_d : numbers of data point
 n : parameter for adsorption isotherm
 P : total pressure
 p_i : partial pressure of component i
 q : amount of adsorbed
 q_{cal} : calculated value of adsorbed amount
 q_{exp} : experimental value of adsorbed amount

Greek Letter

Γ_n, Γ_{ij} : parameters for statistical thermodynamic model

Subscript

i, j : of component i, j

Abbreviation

AD : average percent deviation

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