Pure and Binary Adsorption Isotherms of Nitrogen and Oxygen on Zeolite 5A

Masoud Mofarahi* and Majid Seyyedi

Chemical Engineering Department, Engineering Faculty, Persian Gulf University, Shahid Mahini St. Bushehr, Iran

Adsorption isotherms were measured for pure nitrogen, oxygen, and their binary mixtures (20 %, 40 %, and 60 % nitrogen in the mixture) on a commercial zeolite 5A. The measurements were conduced using a volumetric method at temperatures of (273, 283, 303, and 343) K and at pressures to 950 kPa. The 2D equations of state of van der Waals, Soave–Redlich–Kwong, Peng–Robinson, and Eyring have been applied to represent total adsorption for the pure and binary systems. The amount of adsorption of each component has been obtained in the mixture as well as the selectivity by thermodynamic prediction. Experimental results indicate a very good agreement with thermodynamic modeling and with some current results in the literature.

Introduction

The growing interest in applying adsorption techniques for air separation has been mainly generated by the recent developments in the use of molecular sieves. Pure and multicomponent adsorption data are necessary information for designing a separation process on the basis of adsorption. Experimental collection of adsorption equilibrium data of a mixture is a very tedious and time-consuming process. Therefore, it is preferable to estimate the multicomponent adsorption equilibrium on the basis of the adsorption isotherms of pure components.

With the presentation of new industrial adsorbents, it seems to be necessary to determine their properties for separation systems. Oxygen and nitrogen separation from air on the basis of an adsorption method is one of the well-known processes of adsorption that is commonly performed with pressure swing adsorption on a zeolite 5A bed.¹ Zeolite 5A is commonly used for gas separation by size exclusion. The size cage of calcium zeolite 5A has an internal volume of 776 Å, formed by a cubic lattice of sodalites. The free aperture of the pore is 4.2 Å, allowing for the passage of molecules with a kinetic diameter of < 4.9 Å. It has been found that alkaline earth X zeolites are very selective for N2 adsorption because of the strong interactions between the quadruple moment of N₂ and the cation positioned in the zeolite supercage.^{2,3} Nowadays, zeolite 5A has been used in various chemical processes, in particular, in adsorption. Among them, we can refer to branched paraffin separation from normal paraffin.⁴

Pure and mixed equilibrium data for zeolite 5A are available in the literature in the specific range of temperature and pressure.^{5,6} In this study, we present pure and mixed equilibrium data of the oxygen and nitrogen on a zeolite 5A adsorbent. The total amount of adsorbed oxygen and nitrogen mixture was directly measured by experiments, and the amount of each species adsorbed was predicted by thermodynamic modeling.

Such data have never been previously published. Furthermore, equilibrium data are measured over an extended range of temperature (273 to 343) K.

We used 2D equations of state, which have been expressed by Zhau et al. for pure component data correlation as well as

* Corresponding author. E-mail: mofarahi@pgu.ac.ir. Fax: +98 771 4545188.

mixture adsorption isotherm prediction.⁷ Four well-known equations of state, van der Waals (VDW), Soave–Redlich–Kwong (SRK), Peng–Robinson (PR), and Eyring, were used to correlate and predict the adsorption isotherms. Model constants of the 2D equations of state were determined by pure adsorption isotherms and then applied to predict the adsorption of mixtures by a classical mixing rule. The individual adsorption amount of each component in the mixture as well as the nitrogen selectivity was obtained using performed prediction. The influence of temperature, pressure, and gas composition on the selectivity is discussed.

Theory

If the interfacial region between a gas phase and a solid surface is supposed to be a 2D fluid, then a 2D analog of the 3D equation of state (EOS), using appropriate parameter changes, can be written as follows⁷

$$\left[A\pi + \frac{\alpha\omega^2}{1 + U\beta\omega + W(\beta\omega)^2}\right] [1 - (\beta\omega)^m] = \omega RT \quad (1)$$

where A is the surface area per mass of adsorbent, π is the spreading pressure, ω is the total amount adsorbed per mass of adsorbent, α and β are regressed model constants, R is the gas constant, and T is temperature. The model coefficients, U, W, and m, must be identified to obtain a specific form of the 2D EOS for application. The coefficients are assigned as follows: U = 0, W = 0, and m = 1 for VDW; U = 0, W = 0, and m = 1 for VDW; U = 0, W = 0, and m = 1/2 for Eyring; U = 1, W = 0, and m = 1 for SRK; and U = 2, W = -1, and m = 1 for PR equations of state, as recommended in the literature.⁷

Two-dimensional equations of state can be used to describe adsorbed phases that contain both pure substances and mixtures with the following mixing rules

$$\alpha = \sum_{i} \sum_{j} x_{i} x_{j} \alpha_{ij} \tag{2}$$

$$\beta = \sum_{i} \sum_{j} x_{i} x_{j} \beta_{ij} \tag{3}$$

The fugacity coefficient in the mixture can be calculated with following thermodynamic equation

$$\ln(\hat{\phi}_{i}^{a}) = \int_{0}^{\omega} \left\{ \frac{1}{RT\omega} \left[\frac{\partial(A\pi)}{\partial\omega_{i}} \right]_{T,M_{a},n_{j}} - \frac{1}{\omega} \right\} d\omega - \ln(Z_{a})$$
(4)

where M_a is adsorbent mass and Z_a is a compressibility factor, which is defined by

$$Z_{\rm a} = \frac{a\pi}{RT} = \frac{A\pi}{RT\omega} \tag{5}$$

where a is the specific molar area. Substitution of eq 1 into eq 4 yields the fugacity expression

$$\ln(\hat{\phi}_i) = \frac{2\sum_j \beta_{ij}\omega_j - \beta\omega}{(\beta\omega)^{1-m} - \beta\omega} - \frac{1}{m}\ln[1 - (\beta\omega)^m] - \ln(Z_2) + T_1 + T_2 \quad (6)$$

where

$$T_{1} = -\frac{2\alpha \sum_{j} \beta_{ij} - \alpha \beta \omega}{RT\beta [1 + U\beta \omega + W(\beta \omega)^{2}]}$$
(7)

$$T_{2} = -\frac{\alpha\beta\omega + 2\beta\sum_{j} \alpha_{ij}\omega_{j} - 2\alpha\sum_{j} \beta_{ij}\omega_{j}}{RT\beta^{2}\omega(U^{2} - 4W)^{1/2}} \cdot \ln \left| \frac{2 + (U + (U^{2} - 4W)^{1/2})\beta\omega}{2 + (U - (U^{2} - 4W)^{1/2})\beta\omega} \right| (8)$$

Equilibrium calculations of the adsorption mixture will need to solve the equilibrium relationship between the gas and adsorbed phases simultaneously. The equilibrium between an adsorbed phase and a gas phase requires

$$Z_a \hat{\phi}_i \omega_i = k_i^{\hat{f}_i^g} \tag{9}$$

In this relationship, \hat{f}_i^g (component gas fugacity) is considered to be a nonideal gas phase using an EOS. By extracting logarithms from both sides of the equation, we finally have a general equation as follows

$$F_{i}(\omega_{1},...,\omega_{N_{c}}) = \ln(\omega_{i}) + \frac{2\sum_{j}\beta_{ij}\omega_{j} - \beta\omega}{(\beta\omega)^{1-m} - \beta\omega} - \frac{1}{m}\ln(1 - (\beta\omega)^{m}) + T_{1} + T_{2} - \ln(k_{i}\hat{f}_{i}^{g})$$
(10)

In the above equation, F_i in the equilibrium state would be 0.

Supplied with experimental adsorption data for pure *i*, we can use the above equilibrium relation and fugacity equations for the adsorbed and gas phases for pure *i* to obtain the model pure constants α_i , β_i , and k_i . Thus, for pure substances, the EOS is a three-parameter model. Pure component parameters for the 2D EOS models are determined by minimizing the following objective function

$$\% \text{ AAD} = \frac{100}{\text{NPTS}} \sum_{i}^{\text{NPTS}} \frac{|\omega_i^{\text{(calcd)}} - \omega_i^{\text{(exptl)}}|}{\omega_i^{\text{(exptl)}}}$$
(11)

In this equation, $\omega_i^{\text{(calcd)}}$ and $\omega_i^{\text{(exptl)}}$ are the calculated and experimental amounts of adsorbed component *i*, respectively. NPTS is the number of experimental points.

The percentage of absolute average deviations is carried out over the entire data range for every pure component or binary mixture at a particular temperature. Applying pure substance parameters and mixing rules in conjunction with fugacity



Figure 1. Schematic diagram of the adsorption apparatus.

Table 1. Pure Adsorption Isotherm Data for Nitrogen on Zeolite5A

2	273 K	2	83 K	3	03 K	343 K	
P_{abs}	q	P_{abs}	q	P_{abs}	q	$P_{\rm abs}$	q
kPa	$mol \cdot kg^{-1}$	kPa	$mol \cdot kg^{-1}$	kPa	$mol \cdot kg^{-1}$	kPa	mol•kg ⁻¹
5.6	0.0310	6.1	0.0310	4.2	0.0086	12.1	0.0130
11.0	0.0736	10.8	0.0572	13.0	0.0299	26.0	0.0289
22.1	0.1521	26.8	0.1411	33.3	0.0866	47.8	0.0533
46.2	0.2997	58.5	0.2816	63.4	0.1674	75.8	0.0844
79.0	0.4537	90.9	0.4009	88.7	0.2300	115.9	0.1329
117.2	0.6036	146.5	0.5721	117.5	0.2994	207.1	0.2264
208.1	0.8839	228.7	0.7777	162.5	0.3934	360.0	0.3639
347.3	1.1820	367.6	1.0405	208.5	0.4848	577.9	0.5268
508.8	1.4282	562.0	1.3110	303.8	0.6450	833.1	0.6899
655.9	1.6039	828.4	1.5704	427.0	0.8280	935.2	0.7692
850.8	1.7869	946.7	1.6654	609.5	1.0588		
945.8	1.8673			776.6	1.2249		
				919.0	1.3472		

coefficient equations by the aid of auxiliary equilibrium relations results in attaining the adsorption of individual components in a mixture in terms of the generalized 2D EOS.^{7,8}

Materials and Experimental Method

Materials. Zeolite 5A was provided by Zeochem (Switzerland). They are spherical beads with 3 mm apparent diameter and a BET surface of (457 to 600) $m^2 \cdot g^{-1}$. The gases that have been used in this work and their purities are He (99.99 %), O₂ (99.95 %), and N₂ (99.99 %). They have been supplied by Bushehr Lian Oxygen (Iran).

Apparatus and Procedure. The adsorption apparatus shown in Figure 1 is based on the static volumetric method. There is an adsorption cell and a loading cell. To minimize the dead volume as much as possible, 1/8 in. tubes and 1/8 in. valves were used. The adsorption cell, loading cell, and dead volumes were measured using helium gas. The total amount of gas introduced and recovered in the system was determined by appropriate pressure, temperature, and volume measurements. The temperature in each cell was measured by a K-type thermocouple operated with a precision of 0.01 K; the pressure was measured with a pressure transducer. Temperatures and pressures were recorded at constant time intervals with a recorder (Logoscreen 50, Jumo). During measurement, the adsorption cell was immersed in a water bath (MC 12, Julabo Tech.) maintained at \pm 0.02 K via a refrigeration circulator. Prior to each isotherm measurement, zeolite 5A particles were regenerated in an oven overnight (300 °C for 6 h) under a vacuum of less than 0.05 mbar.

918 Journal of Chemical & Engineering Data, Vol. 54, No. 3, 2009

 Table 2. Pure Adsorption Isotherm Data for Oxygen on Zeolite 5A

273 K		283 K		3	03 K	343 K		
P_{abs}	q	P_{abs}	q	$P_{\rm abs}$	$P_{\rm abs}$ q		q	
kPa	mol•kg ⁻¹	kPa	$mol \cdot kg^{-1}$	kPa	$mol \cdot kg^{-1}$	kPa	mol•kg ⁻¹	
9.2	0.0154	7.9	0.0100	8.6	0.0100	8.0	0.0014	
18.6	0.0362	18.8	0.0270	18.8	0.0226	21.6	0.0109	
34.1	0.0679	32.9	0.0491	33.2	0.0372	43.7	0.0237	
60.0	0.1170	60.7	0.0893	61.3	0.0679	93.0	0.0522	
94.8	0.1790	94.2	0.1411	96.1	0.1022	131.5	0.0777	
141.1	0.2563	141.3	0.2094	143.2	0.1504	212.3	0.1205	
210.6	0.3683	212.4	0.3089	214.8	0.2138	373.4	0.2098	
348.0	0.5670	352.5	0.4866	355.9	0.3455	580.0	0.3165	
537.9	0.7991	541.7	0.7054	548.2	0.5089	826.2	0.4366	
741.3	1.0268	742.7	0.9063	747.9	0.6830	948.4	0.5010	
854.5	1.1652	859.0	1.0179	859.0	0.7679			
934.4	1.2366	936.3	1.0893	931.7	0.8348			

The adsorption equilibrium state was considered to be when the temperatures and the pressures per cell were constant. Temperatures and pressures before and after the adsorption equilibrium state were recorded. The experiment was conducted on a continuous basis at pressures up to 950 kPa. The amount adsorbed was calculated from the temperature and pressure before and after the adsorption equilibrium state by the use of a mass balance.

Discussion and Results

Isotherm of Pure Adsorption. Adsorption isotherms of pure oxygen and nitrogen measured at four temperatures (273, 283, 303, and 343) K are presented in Tables 1 and 2 and are plotted in Figure 2. The adsorption isotherm data were correlated by the VDW, SRK, PR, and Eyring models. The correlated parameters and error of analysis are given in Tables 3 and 4.

Table 3. Regression Results for Pure Nitrogen Adsorption on Zeolite $5\mathrm{A}$

model	α_i	β_i	$\ln(k_i)$	% AAD				
Nitrogen at 273 K								
PR	-7389.8	0.0592	-0.257	5.3				
SRK	-7812.7	0.0109	-0.265	4.8				
Eyring	-4083.4	0.0230	-0.134	6.9				
WDV	-2927.5	0.1726	-0.282	3.7				
	N	itrogen at 283	Κ					
PR	-5713.9	0.1322	-0.537	2.2				
SRK	-5267.3	0.1294	-0.542	1.9				
Eyring	-7612.0	0.0009	-0.499	2.5				
WDV	-2982.5	0.1707	-0.584	1.3				
	N	itrogen at 303	Κ					
PR	4437.4	0.2549	-1.331	4.5				
SRK	4846.3	0.2696	-1.334	4.6				
Eyring	-5530.9	0.0002	-1.239	6.2				
WDV	4230.0	0.2778	-1.326	4.7				
	N	itrogen at 343	Κ					
PR	-5039.9	0.0462	-2.169	2.3				
SRK	-2618.4	0.1197	-2.170	2.3				
Eyring	-5564.8	0.0004	-2.147	2.5				
WDV	-1691.6	0.1419	-2.171	2.2				

As can be seen from these data, the isotherm data are well correlated by all models. The data in Tables 3 and 4 exhibit the good ability of the EOS models to describe the pure oxygen and nitrogen isotherms. Correlation results of all models show that the obtained average error is less than 7 % for pure nitrogen and less than 12 % for pure oxygen. A comparison of the experimental data with the correlation results for pure oxygen and nitrogen adsorption isotherms is illustrated in Figure 2. As shown in Figure 2, the equilibrium loading on zeolite 5A is higher for nitrogen than for oxygen at all temperatures. In



Figure 2. Measured and correlated adsorption isotherms on zeolite 5A: \blacktriangle , nitrogen; O, oxygen. (a) Isotherms at 273 K: -, VDW model; (b) isotherms at 283 K: -, Eyring model; (c) isotherms at 303 K: -, SRK model; and (d) isotherms at 343 K: -, PR model.

model β_i $\ln(k_i)$ % AAD α_{i} Oxygen at 273 K PR 1165.8 0.1772 -1.6272.9 SRK 1064.2 2.8 0.1772 -1.62717 235.3 0.2240 -1.2836.0 Eyring WDV 938.8 0.1772 -1.6272.8 Oxygen at 283 K 2842.4 PR 0.1804 -1.8962.5 SRK 2268.5 0.1710 -1.8942.6 Eyring -1002.30.0030 -1.8593.9 WDV 2125.5 0.1752 -1.8932.7 Oxygen at 303 K PR 726.5 0.1619 -2.1822.8 SRK 1787.4 0.1937 -2.1843.0 Eyring 432.9 0.0124 -2.1231.3 WDV -3572.5 0.0118 -2.1802.6 Oxygen at 343 K PR -7674.80.1097 -2.67411.5 SRK -5998.30.1595 -2.67411.5 Eyring 10 980.9 0.0816 -2.6216.8 WDV -7072.90.1216 -2.67111.7

Table 4. Regression Results for Pure Oxygen Adsorption on Zeolite

5A

particular, this difference is much higher at low temperature. However, each of the four equations of state is in good agreement with the experimental data, as shown in the Figure.

Heat of Adsorption. The adsorption isotherms of nitrogen and oxygen on zeolite 5A considered at four temperatures were employed in evaluating the adsorption enthalpy. For this purpose, the Clausius-Clapeyron equation was applied to the isotherm data at the four temperatures. Therefore, the isosteric heat of adsorption (ΔH) was estimated by means of the linear dependency of $\ln(P)$ on 1/T at constant loading. The heat of the adsorption dependency on adsorption coverage of both gases is shown in Figure 3. The heats of adsorption of oxygen and nitrogen decreased with the increasing degree of coverage. The isosteric heat of adsorption of nitrogen is higher than that of oxygen, especially at a low degree of surface coverage. We note that the adsorption of nitrogen is heterogeneous because the isosteric heat of adsorption decreases with increased loading. However, the heat of adsorption of oxygen slightly decreases with increased loading. Therefore, oxygen adsorption on zeolite 5A is only slightly heterogeneous. Talu⁵ and Mathias⁹ observed the same results, as shown in Figure 3 for another type of zeolite 5A.

Mixture Gas Adsorption. The adsorption separation ability of zeolite 5A was estimated using an indirect method. In this work, the total amount of adsorbed mixture was measured, and the individual adsorption of components was obtained from



Figure 3. Heat of adsorption of nitrogen (---) and oxygen (---) on zeolite 5A as a function of adsorbent loading.

Table 5. Total Amount of Binary Adsorption Isotherm of 20 % Nitrogen on Zeolite 5A

2	73 K	2	283 K 303 K 343		43 K		
$P_{\rm abs}$	q	P_{abs}	q	P_{abs}	q	$P_{\rm abs}$	q
kPa	$mol \cdot kg^{-1}$	kPa	$mol \cdot kg^{-1}$	kPa	$mol \cdot kg^{-1}$	kPa	mol•kg ⁻¹
7.7	0.0240	7.6	0.0211	9.0	0.0166	9.1	0.0095
17.4	0.0515	17.4	0.0476	18.2	0.0325	22.6	0.0194
31.4	0.0900	31.4	0.0787	32.6	0.0520	34.2	0.0263
58.3	0.1575	58.5	0.1381	60.2	0.0893	61.9	0.0466
91.9	0.2378	92.9	0.2081	97.5	0.1326	96.2	0.0727
140.7	0.3538	139.1	0.3035	140.7	0.1917	144.8	0.1058
208.8	0.4965	209.2	0.4418	213.0	0.2841	217.1	0.1571
345.4	0.7437	347.5	0.6601	353.5	0.4418	362.3	0.2453
536.8	1.0271	540.5	0.9108	550.3	0.6259	554.8	0.3561
740.6	1.2661	745.0	1.1157	752.6	0.7972	756.3	0.4731
856.7	1.3839	864.3	1.2262	867.1	0.8789	864.2	0.5314

Table 6. Total Amount of Binary Adsorption Isotherm of 40 % Nitrogen and 60 % Nitrogen on Zeolite 5A

40 % nitrogen				60 % nitrogen					
273 K		303 K		2	83 K	343 K			
$P_{\rm abs}$	q	P_{abs}	q	P_{abs}	q	P_{abs}	q		
kPa	$mol \cdot kg^{-1}$	kPa	$mol \cdot kg^{-1}$	kPa	$mol \cdot kg^{-1}$	kPa	mol•kg ⁻¹		
7.1	0.0259	8.3	0.0145	7.6	0.0252	10.2	0.0140		
16.2	0.0649	11.3	0.0205	17.0	0.0577	18.7	0.0219		
29.8	0.1177	19.0	0.0360	30.8	0.1025	33.0	0.0363		
58.0	0.2105	31.9	0.0578	55.8	0.1776	61.4	0.0618		
89.5	0.3149	56.3	0.1057	90.3	0.2712	96.7	0.0926		
133.9	0.4451	92.8	0.1731	137.1	0.3861	139.2	0.1304		
204.4	0.6291	140.2	0.2530	207.1	0.5401	216.4	0.1889		
341.8	0.9047	211.1	0.3648	341.7	0.8170	357.5	0.3057		
534.5	1.1945	350.9	0.5520	538.6	1.1118	551.4	0.4420		
742.1	1.4479	544.1	0.7688	739.2	1.3344	751.5	0.5799		
854.2	1.5540	749.3	0.9560	854.3	1.4452	860.0	0.6427		
		855.0	1.0462	933.3	1.5319	944.8	0.7004		

Table 7. Comparison of Predictions Error of Models for Different $N_2 / O_2 \mbox{ mixtures}$

	20 % n	itrogen		40 % n	itrogen	60 % nitrogen	
273 K	283 K	303 K	343 K	273 K	303 K	283 K	343 K
3.0	7.0	9.8	5.2	3.0	6.5	7.6	8.6
7.6	6.3	6.1	6.2	8.2	5.0	9.0	7.4
3.1 2.6	6.2 6.1	7.0 7.1	5.3 5.2	4.8 3.0	5.5 5.4	8.5 8.5	8.7 8 7
	273 K 3.0 7.6 3.1 2.6	20 % n 273 K 283 K 3.0 7.0 7.6 6.3 3.1 6.2 2.6 6.1	20 % nitrogen 273 K 283 K 303 K 3.0 7.0 9.8 7.6 6.3 6.1 3.1 6.2 7.0 2.6 6.1 7.1	20 % nitrogen 273 K 283 K 303 K 343 K 3.0 7.0 9.8 5.2 7.6 6.3 6.1 6.2 3.1 6.2 7.0 5.3 2.6 6.1 7.1 5.2	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	20 % nitrogen 40 % nitrogen 273 K 283 K 303 K 343 K 273 K 303 K 3.0 7.0 9.8 5.2 3.0 6.5 7.6 6.3 6.1 6.2 8.2 5.0 3.1 6.2 7.0 5.3 4.8 5.5 2.6 6.1 7.1 5.2 3.0 5.4	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$

thermodynamic prediction. The total adsorbed amount of the 20 % nitrogen mixture on zeolite 5A at temperatures of (273, 283, 303, and 343) K are presented in Table 5. In Table 6, the total amount adsorbed for two mixtures of 40 % nitrogen and 60 % nitrogen on zeolite 5A at different temperature is listed. Table 7 gives average errors of model predictions for different mixtures. It can be observed in Table 7 that all models provide very similar prediction with acceptable accuracy for every binary mixture, and the worst error in the predictions is less than 10 %. Figure 4 presents comparisons with measured data and the PR EOS model prediction for the 20 % nitrogen binary system. The model utilizes the parameters reported in Tables 3 and 4. As can be noted from Figure 4, the prediction results show a good agreement with measured values. The adsorption equilibrium isotherms of the 40 % nitrogen mixture at (273 and 303) K and 60 % nitrogen at (283 and 343) K are shown in Figures 4 and 5, respectively. As can be seen in these Figures, the prediction results using the VDW EOS for 60 % nitrogen and the SRK EOS for 40 % nitrogen show good agreement with measured value. As shown in Figures 4, 5, and 6, the pure substance constants that have been obtained from the correlation of the adsorption pure data with mixing rules appropriately predict the binary adsorption equilibrium data.



Figure 4. Total amount of adsorption isotherms for N_2/O_2 20:80 mixture: •, 273 K; \blacktriangle , 283 K; \blacklozenge , 303 K; \blacksquare , 343 K; \neg , prediction by PR model.



Figure 5. Total amount of adsorption isotherms for N_2/O_2 60:40 mixture: •, 283 K; \blacktriangle , 343 K; -, prediction by VDW model.



Figure 6. Total amount of adsorption isotherms for N_2/O_2 40:60 mixture: •, 273 K; \blacktriangle , 303 K; -, prediction by SRK model.

Predicted N_2/O_2 **Selectivity.** Binary gas adsorption involves three degrees of freedom: temperature, pressure, and gas composition. In this Article, N_2/O_2 selectivity and solid phase composition were estimated by thermodynamic prediction to study the influences of temperature, pressure, and gas composition on nitrogen/oxygen separation. For this purpose, the VDW model is applied to the prediction in this section.

Figure 7 presents the N_2/O_2 selectivity at 273 K and pressures of (1, 3, and 9) bar in terms of gas composition.

The selectivity is defined as following

$$S_{N_2,O_2} = \frac{x_{N_2}/x_{O_2}}{y_{N_2}/y_{O_2}}$$
(12)

where x_{N_2} , x_{O_2} , y_{N_2} and y_{O_2} are the mole fractions of N₂ and O₂ in adsorbed and gas phases at equilibrium, respectively. As can



Figure 7. Predicted N₂/O₂ selectivity at 273 K as a function of gas composition. Total pressure: \blacktriangle , 9 bar; \blacksquare , 3 bar; \blacklozenge , 0.1 bar.



Figure 8. Predicted N₂/O₂ selectivity at 273 K as a function of pressure. Gas phase composition: \blacktriangle , 0.9; \blacksquare , 0.4; \blacklozenge , 0.1.



Figure 9. Predicted adsorbed phase versus gas phase composition at 5 bar. Temperature: ▲, 283 K; ■, 303 K; ●, 343 K.

be observed, decreasing the nitrogen mole fraction in the gas phase increases the N_2/O_2 selectivity, and the selectivity is higher at the lower pressures. Figure 8 provides another view of N₂/ O₂ predicted selectivity at 273 K and three different nitrogen gas compositions (0.1, 0.4, and 0.9) as a function of pressure. These effects demonstrate that the first set of adsorbent sites is highly selective to nitrogen over oxygen. As can be observed from Figure 7, the predicted selectivity increases from about 2 at the nitrogen-rich end to 3.5 for compositions rich in oxygen. The same result as that above has been seen for nitrogen adsorption selectivity over zeolite 5A by Talu⁵ and Mathias.⁹ The x-y diagram, commonly used to display binary adsorption behavior, is shown in Figure 9. This Figure illustrates the predicted adsorbed phase versus nitrogen gas phase composition at 5 bar and three temperatures of (283, 303, and 343) K. Also, this Figure not only shows an ideal form of N₂/O₂ binary gas adsorption but also compares binary gas adsorption behavior

at various temperature. As can be noted from Figure 9, nitrogen separation by solid phase at low temperature is higher than that at high temperature.

Conclusions

Experimental isotherms on zeolite 5A for pure nitrogen, oxygen, and several N₂/O₂ mixtures were measured by a volumetric method over a wide range of pressure and temperature. Thermodynamic modeling by 2D EOS is valuable for the analysis and correlation of both pure nitrogen and oxygen adsorption data. With mixing rules, EOS models can be appropriately used to predict N₂/O₂ binary gas adsorption mixtures from the obtained correlated parameters. The error in the adsorption obtained from the prediction is less than 10~%in all cases. N_2/O_2 binary system behavior on the zeolite 5A adsorbent is studied by prediction with 2D EOS. At a fixed pressure and temperature, prediction results show that nitrogen selectivity increases when the nitrogen composition of the gas phase decreases. At a fixed temperature, nitrogen selectivity will increase in the gas phase when nitrogen pressure decreases for a specified mole fraction. Furthermore, prediction results show that the lower the temperature at a specified pressure, the greater the nitrogen separation by zeolite 5A.

Literature Cited

 Sircar, S.; Rao, M. B.; Golden, T. C. Fractionation of air by zeolites. Stud. Surf. Sci. Catal. 1999, 120, 395–423.

- (2) Jayaraman, A.; Yang, R. T. Stable oxygen-selective sorbents for air separation. *Chem. Eng. Sci.* 2005, 60, 625–634.
- (3) Grande, C. A.; Gigola, C.; Rodrigues, A. E. Adsorption of propane and propylene in pellets and crystals of 5A zeolite. *Ind. Eng. Chem. Res.* 2002, *41*, 85–92.
- (4) Ackley, M. W.; Rege, S. U.; Saxena, H. Application of natural zeolites in the purification and separation of gases. *Microporous Mesoporous Mater.* 2003, 61, 25–42.
- (5) Talu, O.; Li, J.; Kumar, R.; Mathias, P. M.; Moyer, J. D.; Schork, J. M. Measurement and analysis of oxygen/nitrogen/5A-zeolite adsorption equilibria for air separation. *Fuel Energy Abstr.* **1996**, *37*, 149–159.
- (6) Sorrel, G. A.; Granville, W. H.; Daly, W. O. Adsorption equilibria for oxygen and nitrogen gas mixtures on 5A molecular sieves. *Chem. Eng. Sci.* **1983**, *38*, 1517–1523.
- (7) Zhou, C.; Hall, F.; Gasem, A. M.; Robinson, R. L. Predicting gas adsorption using 2D equations of state. *Ind. Eng. Chem. Res.* 1994, 33, 1280–1289.
- (8) Mofarahi, M.; Hashemifard, S. A. Predicting Gas Adsorption Using Covolume Dependent Mixing Rule, Proceedings of the Eleventh International Conference on Properties and Phase Equilibria for Product and Process Design (PPEPPD), Hersonissos, Crete, Greece, May 20-25, 2007.
- (9) Mathias, P. M.; Kumar, R.; Moyer, J. D.; Schork, J. J. M.; Srinivasan, S. R.; Auvil, S. R.; Talu, O. Correlation of multicomponent gas adsorption by the dual-site Langmuir model. Application to nitrogen/ oxygen adsorption on 5A-zeolite. *Ind. Eng. Chem. Res.* **1996**, *35*, 2477– 2483.

Received for review September 17, 2008. Accepted December 14, 2008. We thank the Persian Gulf University research office for financial support, for providing various facilities, and for necessary approval under contract no. 19-209.

JE8006919