Binary and Ternary Adsorption of Methane, Ethane, and Ethylene on Titanosilicate ETS-10 Zeolite

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Binary and ternary equilibrium adsorption data of methane, ethane, and ethylene on titanosilicate ETS-10 zeolites are reported at temperatures of 280 K and 325 K and pressures of 350 kPa and 700 kPa. The experimental data are modeled using the ideal adsorbed solution theory (IAST) in conjunction with the pure isotherms of Toth, Unilan, and Virial. The fit of this model to these data is satisfactory. Values of the relative adsorptivity calculated from the data and the IAST fits of the data show that the separation of methane from ethane or ethylene is extremely feasible at any conditions. Also, the separation of ethane from ethylene is highly favorable on ETS-10, particularly at low temperature. The removal of methane or ethane from the ternary mixture methane + ethane + ethylene is extremely easy at any operating conditions.

Introduction

Adsorptive gas separations involve considerations of adsorbent design, kinetics, and equilibria. The goal of the adsorbent designer is size exclusion of a particular species from the remaining gases in the mixture as for instance in the separation of iso and n paraffins in the PAREX process[1] or more recently as in a U.S. patent on the size exclusion of ethane from ethylene employing CTS titanium silicate molecular sieves.[2] The tuning of molecular sieves to a desired pore size is clearly the goal of adsorbent manufacturers. Kuznicki et al.[3] have used this property to adjust the pore sizes of ETS-4 through systematic dehydration at elevated temperatures to "tune" the effective pores of the crystal. This can be successfully applied to tailor these adsorbents to give size-selective adsorbents for commercially important separations of gas mixtures with similar size in the 3 Å to 4 Å range, such as $N_2 + CH_4$, $Ar + O_2$, and $N_2 + O_2$. Alternatively, it has been known for a long time that the size of pore apertures of zeolites can be systematically controlled by silica deposition on the external surface of the zeolite from a dilute solution of tetraethyl orthosilicate (TEOS) in dry toluene. A recent paper on this avenue is the modification of the 4 Å pore size by Chudasama et al.[4] Much of this work is proprietary, but it is the primary direction of future adsorbent research. Other properties of adsorbents that influence the adsorption are BET surface area, macropore size, crushing strength, and life of the adsorbent.

The kinetics of adsorption may be controlled by film resistance, macropore resistance, micropore resistance, or a pore mouth resistance as elucidated in the book by Karger and Ruthven.[5] Column and pressure swing adsorption (PSA) design must consider these factors carefully to achieve their objectives.

The third primary factor is the thermodynamics of equilibria of the adsorbates on the adsorbents. Different isotherm objectives may exist when considering column design versus PSA design, as in the latter a rectangular isotherm is generally not desirable. The isotherms most typically used are the Langmuir, Freundlich, Langmuir−Freundlich, Toth, and Unilan isotherms. Systematic procedures involving modeling of mixtures of these isotherms are not as well developed as for vapor−liquid equilibria data, although Valenzuela and Myers[6] did systematize the reported data in 1989 using the Toth and Unilan mixture models. The general mixture models may be classified into six groups: (1) the extended Langmuir model; (2) the ideal adsorption solution theory;[7] (3) the vacancy solution theory;[8−10] (4) the statistical thermodynamic models;[11−13] (5) the Polanyi potential theory;[14] and (6) other empirical, semi-theoretical, or theoretical models. Recent papers in some of these areas are as follows: potential theory;[15] potential theory and ideal adsorbed solution;[16] multilayer adsorption,[17] extended Langmuir, ideal adsorbed solution, and vacancy theory;[18] group contribution theory;[19] and multisite model.[20]

In this work, we report on the binary and ternary adsorption of methane, ethane, and ethylene on titanosilicate ETS-10 zeolite at various pressures and temperatures. The collected data are modeled using the ideal adsorbed solution theory in conjunction with the pure component models of Toth, Unilan, and Virial.

Theoretical Background

Several models are reported in the literature to describe the adsorption behavior of a multicomponent system including Langmuir, Toth, and Freundlich models. The ideal adsorbed solution theory (IAST) model is more appropriate for systems comprising species of similar chemical structure such as the systems under study. According to the IAST theory, the multicomponent equilibrium behavior can be predicted from knowledge of the pure component equilibrium corresponding to the mixture using the IAST. This theory[6] presents a relationship between the bulk and the adsorbed phase for the mixtures assuming ideal behavior. Thus, the relationship between the two phases can be described by an analogous form of Raoult's law:

$$Py_i = P_i^\circ x_i \tag{1}$$

where P_i° is the pressure of pure component i which it would exert as a pure component at the same temperature and spreading pressure (π) as those of the mixture. At equilibrium, the

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10.1021/je050364c CCC: $33.50

spreading pressure is constant and can be evaluated from the pure component isotherms according to

$$\frac{\pi A}{RT} = \varphi = \int_0^{P_1^\circ} \frac{q_1}{P_1} \mathrm{d}P_1 = \int_0^{P_2^\circ} \frac{q_2}{P_2} \mathrm{d}P_2 = \cdots = \int_0^{P_i^\circ} \frac{q_i}{P_i} \mathrm{d}P_i \qquad (2)$$

The summation of the adsorbed phase mole fraction is unity:

$$\sum_{i=1}^{N} x_i = 1 \qquad (3)$$

where q_i is the pure component loading. Therefore, if an appropriate pure component model is used in eq 2, the values of P_i° corresponding to each component in the mixture can be calculated. The mole fraction of each component in the mixture can then be obtained from

$$x_i = \frac{Py_i}{P_i^\circ} \qquad (4)$$

The total solid-phase loading (q) is calculated from

$$q = \frac{1}{\displaystyle\sum_{i=1}^{N} \frac{x_i}{q_i^\circ}} \qquad (5)$$

where q_i° is the amount adsorbed for component i in the pure state at P_i°. Valenzuela and Myers[6] presented a general algorithm for solving the IAST equations. This algorithm was adopted in this paper to predict the mixture behavior using the pure models of Toth, Unilan, and Virial (three constant models). The pure component parameters of the three isotherms have been determined in our previous work.[21]

The ease of adsorption separation can be determined from the separation factor or relative adsorptivity (α) defined by:

$$\alpha_{ij} = (y_i/x_i)/(y_j/x_j) \qquad (6)$$

where i refers to the less adsorbed species. The higher the value of α, the better is the separation. Typically, the relative adsorptivity is at least 1 order of magnitude higher than the analogous relative volatility in absorption or distillation for some systems. This illustrates how effective adsorption is in comparison to other separation techniques.

Experimental Procedure

The volumetric method used to collect the pure component data has been extended to collect the binary and tertiary data. The experimental setup and procedure are identical to those reported by Abdul-Rehman and co-workers.[22,23] The properties of the titanosilicate ETS-10 used are the same as those reported by Al-Baghli and Loughlin.[21]

The temperature uncertainty of the thermocouple is ± 0.05 K, but that of the cell system is greater at ± 0.1 K. The pressure uncertainty of the Barocel gauge is ± 0.5 kPa. The greatest uncertainty is in the determination of the mole fraction of the species as this involved both an application of the Soave−Redlich−Kwong equation of state in the loading and adsorbing cell and composition analysis using gas chromatographic techniques. An estimate is ± 0.1 % growing cumulatively at a rate of $[1.001^{i}-1.0]$ where i is the number of the experimental point as the adsorption steps are additive during a continuous series of measurements. As this comes to ± 1.0 % after 10 measurements, the maximum successive steps are limited to 10 or less in any one continuous set of experiments as a result of this cumulative uncertainty.

Table 1. $x-y$ Data on Titanosilicate ETS-10 Zeolite

280 K and 150 kPa		280 K and 500 kPa		325 K and 150 kPa	
x_1	y_1	x_1	y_1	x_1	y_1
System A: Methane (1) + Ethane (2)					
0.008	0.341	0.010	0.361	0.020	0.358
0.026	0.547	0.044	0.581	0.044	0.558
0.050	0.677	0.082	0.717	0.075	0.680
0.079	0.756	0.122	0.804	0.105	0.755
0.109	0.811	0.173	0.860	0.131	0.805
0.133	0.848	0.214	0.895	0.166	0.839
0.156	0.873	0.261	0.919	0.193	0.864
0.177	0.892	0.302	0.934	0.218	0.882
0.208	0.906	0.346	0.945	0.243	0.897
System B: Methane (1) + Ethylene (2)					
0.002	0.347	0.001	0.352	0.009	0.363
0.007	0.552	0.008	0.569	0.018	0.572
0.018	0.684	0.012	0.702	0.026	0.701
0.025	0.768	0.020	0.790	0.035	0.784
0.032	0.826	0.030	0.847	0.044	0.834
0.036	0.865	0.040	0.884	0.052	0.868
0.043	0.891	0.053	0.910	0.063	0.892
0.047	0.909	0.063	0.928	0.073	0.909
0.050	0.923	0.081	0.941	0.087	0.921
System C: Ethane (1) + Ethylene (2)					
0.061	0.275	0.072	0.304	0.138	0.475
0.108	0.459	0.115	0.503	0.198	0.599
0.156	0.584	0.190	0.630	0.249	0.682
0.197	0.672	0.233	0.720	0.295	0.741
0.236	0.734	0.324	0.828	0.340	0.785
0.270	0.780	0.358	0.858	0.381	0.817
0.299	0.813	0.391	0.880	0.417	0.842
0.327	0.839	0.421	0.898	0.450	0.861
0.354	0.860				

Table 2. Pure Component Model Equations[a]

isotherm	model
Vant Hoff	$K_\mathrm{H} = K_\mathrm{o} \exp\left(-\frac{\Delta H}{RT}\right)$
Toth	$q = \frac{q_\mathrm{s} P}{(b + P^t)^{1/t}}$
Toth Henry constant relationship	$K_\mathrm{H} = q_\mathrm{s} b^{-1/t}$
Unilan	$q = \frac{q_\mathrm{s}}{2s} \ln\left[\frac{c + P\exp(s)}{c + P\exp(-s)}\right]$
Unilan Henry constant relationship	$K_\mathrm{H} = \frac{q_\mathrm{s}}{cs} \sinh(s)$
Virial	$P = \frac{q}{K_\mathrm{H}} \exp(A_1 q + A_2 q^2 + \cdots)$

[a] K_H/mol·kg^{-1}·kPa^{-1}, Henry's constant; K_o/mol·kg^{-1}·kPa^{-1}, preexponential factor; $(-\Delta H)$/kJ·mol^{-1}, isosteric enthalpy of adsorption; T/K, temperature; R/kJ·mol^{-1}·K^{-1}, universal gas constant; q/mol·kg^{-1}, loading; q_s/mol·kg^{-1}, saturation concentration; P/kPa, pressure; t/dimensionless, Toth isotherm heterogeneity parameter; b/kPa^t, Toth isotherm equilibrium parameter; c/kPa, Unilan equilibrium parameter; s/dimensionless, Unilan heterogeneity of the surface dimensionless constant; A_i/kg^i·mol^{-i}, virial coefficients.

Results and Discussion

Three different experiments were carried out to examine the adsorption behavior of the binary system methane + ethane on ETS-10 zeolite at various temperatures and pressures. Three runs were performed, two at 280 K and at pressures of 150 kPa and 500 kPa and a third run at 325 K and 150 kPa. The

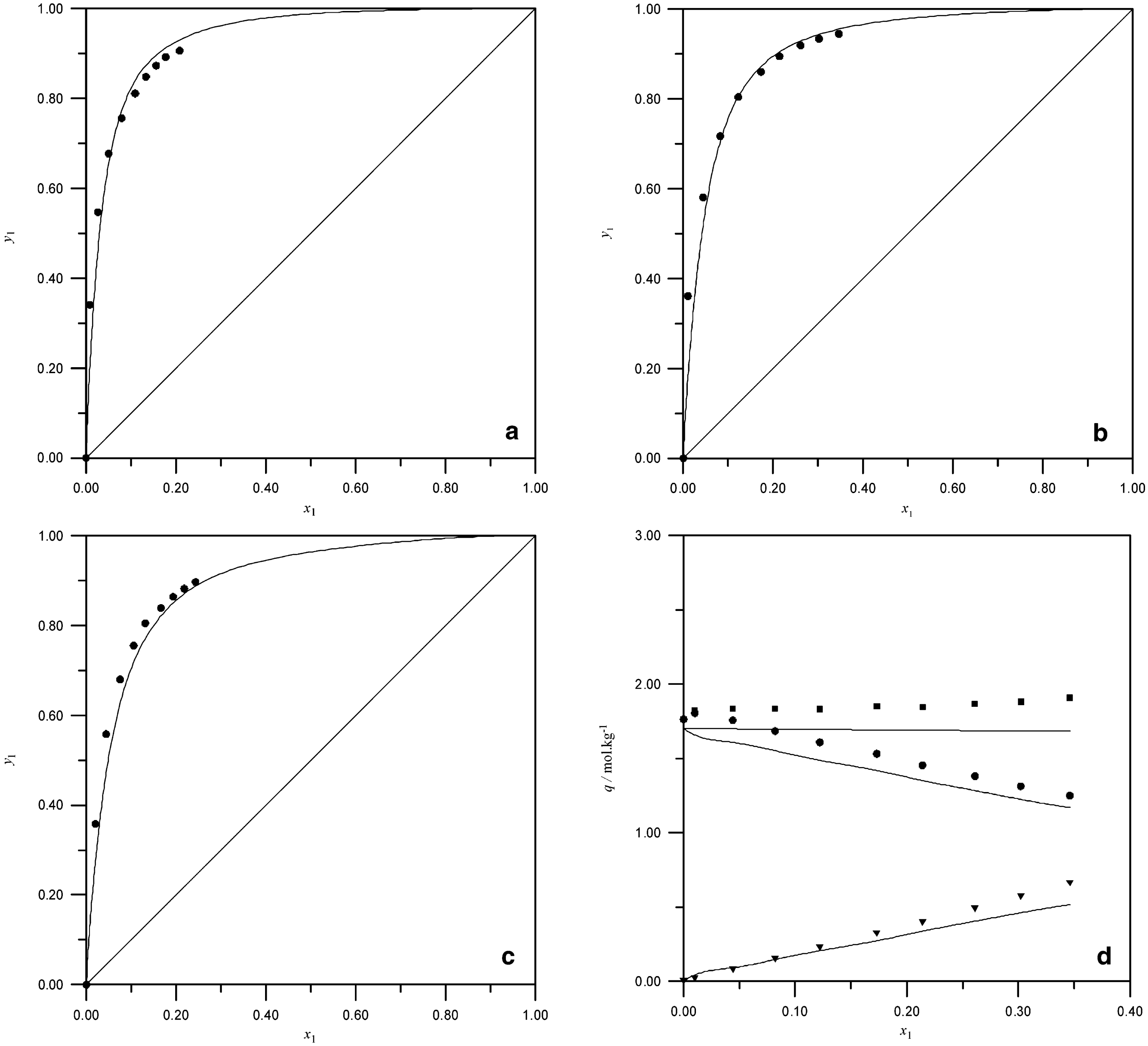

Figure 1. Fit of IAST using Toth isotherm model to the $x-y$ data for methane (1) + ethane (2) (a) at 280 K and 150 kPa, (b) at 280 K and 500 kPa, and (c) at 325 K and 150 kPa. ●, data; y, gas-phase mole fraction; x, adsorbed-phase mole fraction. (d) Fit of IAST using Toth isotherm model to the $x-q$ data for methane (1) + ethane (2) at 280 K and 500 kPa. ▼, methane; ●, ethane; ■, total; x, adsorbed-phase mole fraction; q, amount adsorbed.

Table 3. Parameters Used for Modeling Binary and Ternary Data

Toth Isotherm

sorbate	t	q_s/(mol·kg^{-1})	K_o/(10^6 mol·kg^{-1}·kPa^{-1})	$-\Delta H$/(kJ·mol^{-1})
methane	0.58	2.66	4.3810	21.445
ethane	0.57	1.75	0.9965	35.428
ethylene	0.42	2.00	1.2331	42.795

Unilan Isotherm

sorbate	s	q_s/(mol·kg^{-1})	c/kPa 280 K	c/kPa 325 K	K_o/(10^6 mol·kg^{-1}·kPa^{-1})	$-\Delta H$/(kJ·mol^{-1})
methane	0.58	2.66	207.27	748.05	4.2356	21.049
ethane	0.57	1.75	1.368	14.140	1.5227	34.658
ethylene	0.42	2.00	0.299	2.795	4.7483	33.846

Virial Isotherm

sorbate	A_1/(kg·mol^{-1})	A_2/(kg^2·mol^{-2}) 280 K	A_2/(kg^2·mol^{-2}) 325 K	A_3/(kg^3·mol^{-3}) 280 K	A_3/(kg^3·mol^{-3}) 325 K	K_o/(10^6 mol·kg^{-1}·kPa^{-1})	$-\Delta H$/(kJ·mol^{-1})
methane	0.55	0.00	0.195	0.316	0.259	4.1354	20.784
ethane	0.48	0.00	0.00	1.040	1.032	0.9725	33.846
ethylene	0.27	0.00	0.035	0.858	0.890	5.0614	34.340

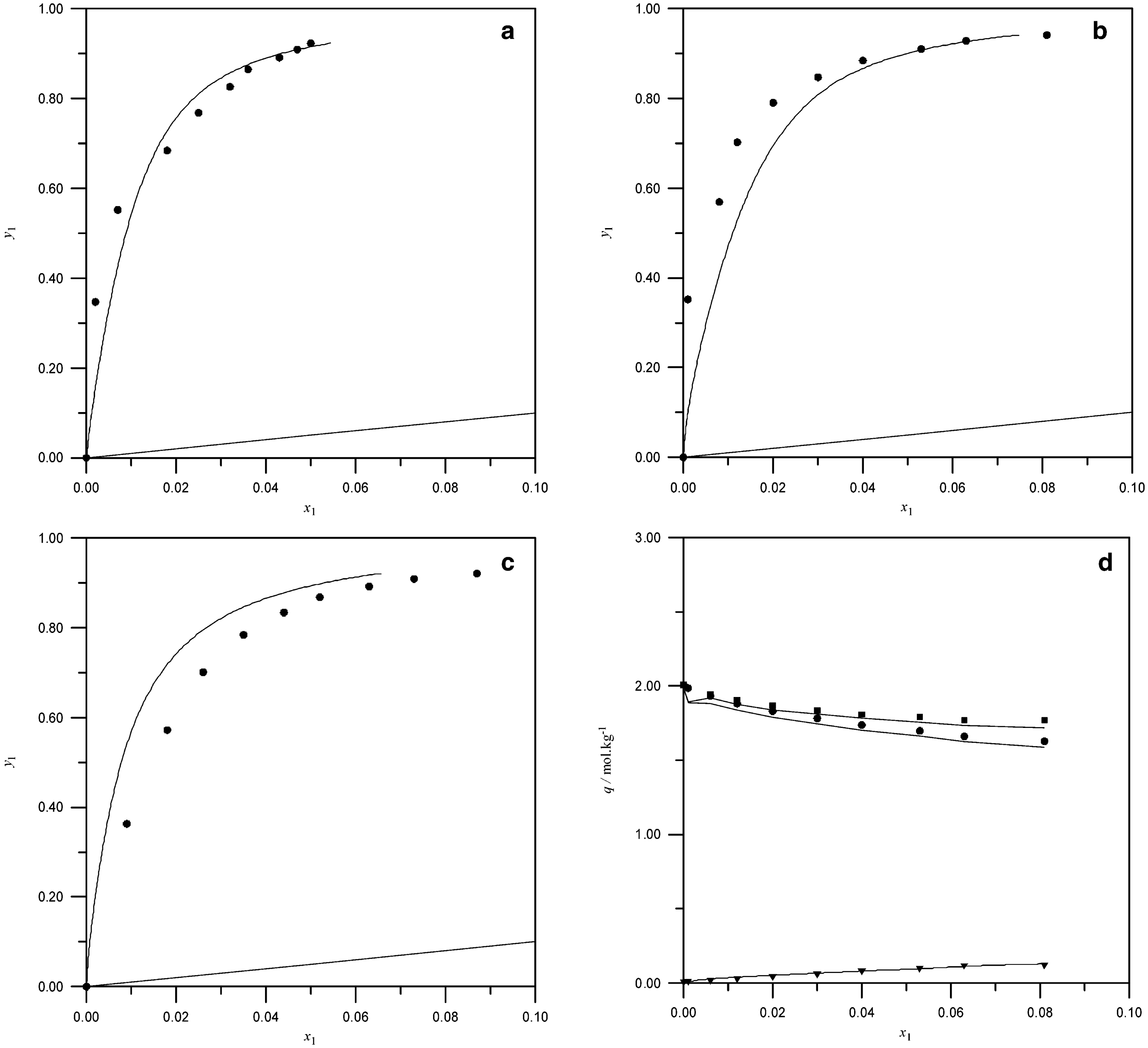

Figure 2. Fit of IAST using Virial isotherm model to the $x-y$ data for methane (1) + ethylene (3) (a) at 280 K and 150 kPa, (b) at 280 K and 250 kPa, and (c) at 325 K and 150 kPa. ●, data; y, gas-phase mole fraction; x, adsorbed-phase mole fraction. (d) Fit of IAST using Virial isotherm model to the $x-q$ data for methane (1) + ethylene (3) at 280 K and 250 kPa. ▼, methane; ●, ethane; ■, total; x, adsorbed-phase mole fraction; q, amount adsorbed.

Table 4. Values of the Relative Adsorptivity for the Binary Systems Methane + Ethane, Methane + Ethylene, and Ethane + Ethylene

		relative adsorptivity			
T/K	*P*/kPa	experimental	IAST-Toth	IAST-Unilan	IAST-Virial
		Methane + Ethane			
280	150	45.23	33.49	34.41	30.40
280	500	30.13	24.39	24.68	20.18
325	150	27.43	20.06	21.53	22.38
		Methane + Ethylene			
280	150	174.79	169.90	179.66	118.39
280	250	163.70	152.19	159.68	95.75
325	150	72.91	122.41	129.69	130.99
		Ethane + Ethylene			
280	150	7.60	9.67	10.56	10.67
280	250	7.79	10.23	11.32	12.38
325	150	5.65	10.33	10.61	8.84

experimental data are all symmetrical and consistent and are tabulated in Table 1 system A. The data were modeled by using the IAST model in conjunction with the pure component models Toth, Unilan, and Virial. The models and the parameters used in the fits are the same as that in the paper of Al-Baghli and Loughlin.[21] For clarity of this presentation, they are reproduced in Tables 2 and 3. An excellent fit has been obtained using the IAST model with Toth, Unilan, and Virial three constant isotherms for the four runs. The ideality of the adsorbed mixture methane+ethane explains the good reproduction obtained with the IAST model. Plots of the adsorbed-phase mole fraction of methane versus the gas-phase mole fraction of methane are presented in Figure 1a−c. These plots indicate that the IAST-Toth combination appears the best among the models used. In addition, the three models support the experimental data that the separation of methane from ethane on ETS-10 is possible at any conditions but is best at low temperature and pressure. The $x-q$ fit for this system is presented in Figure 1d. Comparing the results obtained for this system on ETS-10 to those obtained by Bin Abdul Rehman et al.[22,23] on 13X and 5A zeolites shows that the separation of methane from ethane is more practical on ETS-10 zeolite. The relative adsorptivity values for this system

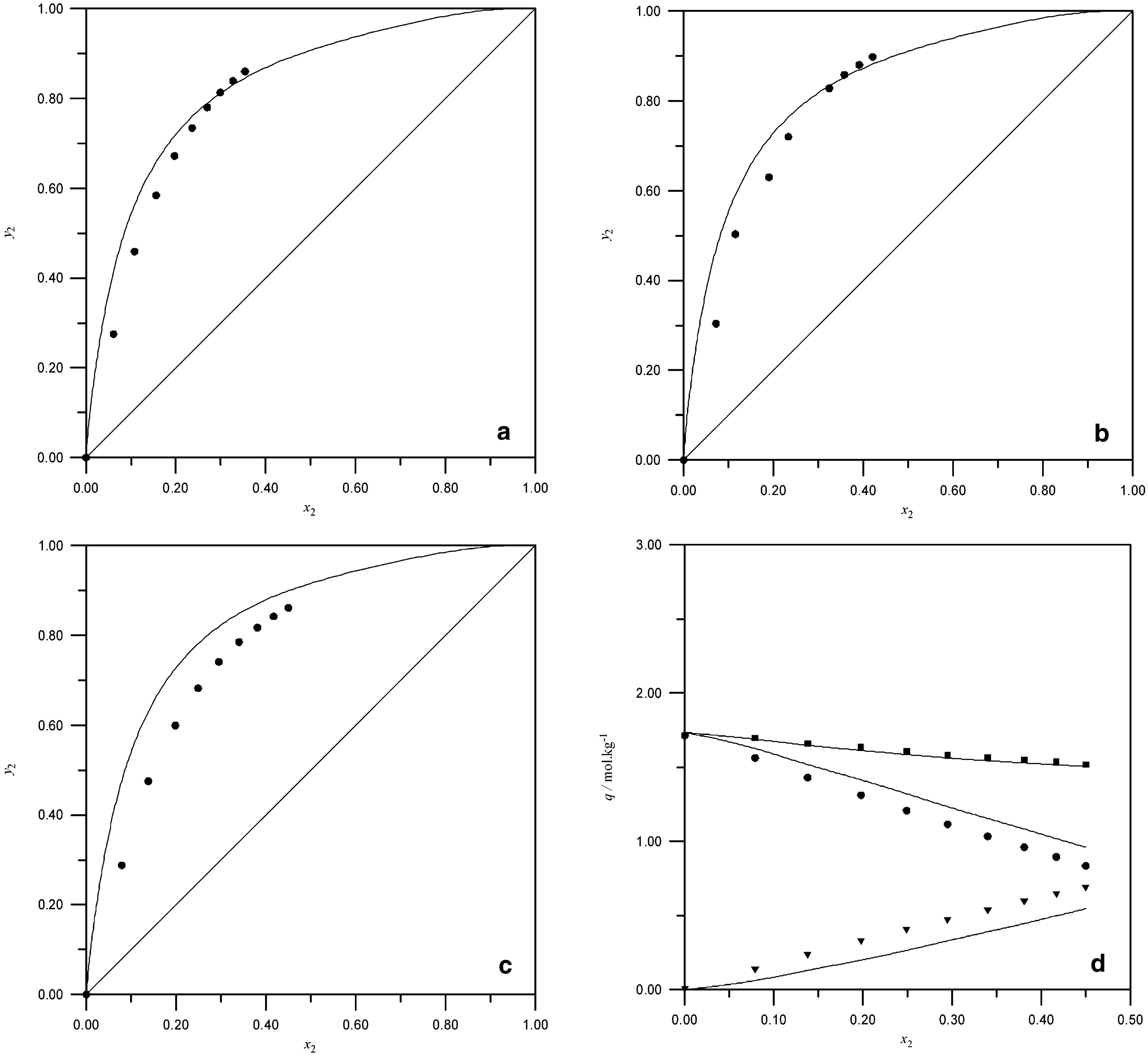

Figure 3. Fit of IAST using Unilan isotherm model to the $x-y$ data for ethane (2) + ethylene (3) (a) at 280 K and 150 kPa, (b) at 280 K and 250 kPa, and (c) at 325 K and 150 kPa. ●, data; y, gas-phase mole fraction; x, adsorbed-phase mole fraction. (d) Fit of IAST using Unilan isotherm model to the $x-q$ data for ethane (2) + ethylene (3) at 325 K and 150 kPa. ▼, methane; ●, ethane; ■, total; x, adsorbed-phase mole fraction; q, amount adsorbed.

are listed in Table 4. These values are calculated using eq 6 at approximately 50 % gas-phase mole fraction of methane. The experimental values are approximately 25 % lower than the theoretical ones despite the fact that the IAST fit is so good and the system is ideal. This result is surprising. A possible explanation is the deviation in the predicted adsorbed phase loadings as observed in Figure 1d, which is higher than exists for the other systems.

The methane−ethylene system has been examined at three different conditions, namely, 280 K and 150 kPa, 280 K and 250 kPa, and 325 K and 150 kPa. The data are tabulated in Table 1, system B. The $x-y$ fits to the data are presented in Figure 2a−c while the $x-q$ plot is shown in Figure 2d. Their appears to be a larger deviation in the predicted fits in Figures 2 b−c than in the previous case. This is probably due to magnification of the x scale to 10 % of the total, which will magnify any discrepancy. It may also reflect the fact that a binary involving ethylene may be less ideal than the alkanes system only. The results obtained indicate that methane is very weakly adsorbed in the presence of ethylene; therefore, a separation can be achieved easily at any conditions but is best at low temperature and pressure. This conclusion is supported by the high values of the relative adsorptivity reported for this system in Table 4.

Three experiments at the same conditions of the previous system were obtained for the binary system ethane-ethylene. The data, tabulated in Table 1c, and the fits of the data are shown in Figure 3. The results show that ethane adsorption on ETS-10 is weak in the presence of ethylene, which indicates that ETS-10 is a highly appropriate adsorbent for the separation of ethane from ethylene. This conclusion is supported by the three models used to fit the experimental data for this system (IAST-Toth, IAST-Unilan, and IAST-Virial). The fit is not as good as for the first system, probably reflecting the fact that a binary involving ethylene may be less ideal than the alkanes system only. Values of the relative adsorptivity for this system are listed in Table 4. Comparing these values with the values obtained for ethane-ethylene on SR-115 zeolite (Al-Baghli[24]) shows that

Table 5. *x*−*y* Fit of IAST Model Using Toth, Unilan, and Virial Isotherms for the Ternary System Methane (1) + Ethane (2) + Ethylene (3) at 300 K and 200 kPa

		experimental		IAST-Toth		IAST-Unilan		IAST-Virial	
y_1	y_2	x_1	x_2	x_1	x_2	x_1	x_2	x_1	x_2
0.000	0.000			0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.000	0.236	0.000	0.051	0.0000	0.0209	0.0000	0.0194	0.0000	0.0178
0.359	0.147	0.009	0.051	0.0062	0.0207	0.0062	0.0193	0.0084	0.0188
0.575	0.094	0.012	0.049	0.0133	0.0201	0.0132	0.0187	0.0168	0.0195
0.707	0.062	0.026	0.046	0.0214	0.0193	0.0210	0.0178	0.0257	0.0197
0.792	0.042	0.034	0.043	0.0305	0.0183	0.0297	0.0168	0.0357	0.0196
0.847	0.030	0.047	0.040	0.0406	0.0177	0.0391	0.0161	0.0470	0.0197
0.882	0.022	0.055	0.037	0.0506	0.0166	0.0483	0.0150	0.0586	0.0189
0.907	0.017	0.068	0.034	0.0616	0.0161	0.0582	0.0144	0.0717	0.0187
0.924	0.013	0.077	0.031	0.0718	0.0148	0.0673	0.0131	0.0841	0.0173
0.936	0.010	0.083	0.029	0.0812	0.0132	0.0756	0.0116	0.0956	0.0156
1.000	0.000			1.0000	0.0000	1.0000	0.0000	1.0000	0.0000

Table 6. *x*−*q* Fit of IAST Model Using Toth, Unilan, and Virial Isotherms for the Ternary System Methane (1) + Ethane (2) + Ethylene (3) at 300 K and 200 kPa

		experimental			IAST-Toth			IAST-Unilan			IAST-Virial		
x_1	x_2	q_1	q_2	q_3	q_1	q_2	q_3	q_1	q_2	q_3	q_1	q_2	q_3
0.000	0.000				0.000	0.000	1.858	0.000	0.000	1.911	0.000	0.000	1.870
0.000	0.051	0.000	0.094	1.751	0.000	0.039	1.802	0.000	0.037	1.851	0.000	0.033	1.810
0.009	0.051	0.016	0.094	1.716	0.011	0.038	1.766	0.011	0.036	1.804	0.015	0.034	1.753
0.012	0.049	0.022	0.087	1.664	0.024	0.036	1.728	0.024	0.034	1.752	0.030	0.034	1.699
0.026	0.046	0.045	0.081	1.619	0.038	0.034	1.689	0.037	0.032	1.699	0.044	0.034	1.648
0.034	0.043	0.059	0.074	1.579	0.053	0.032	1.648	0.051	0.029	1.645	0.060	0.033	1.599
0.047	0.040	0.079	0.067	1.540	0.069	0.030	1.605	0.066	0.027	1.592	0.078	0.033	1.550
0.055	0.037	0.091	0.061	1.503	0.085	0.028	1.567	0.080	0.025	1.545	0.096	0.031	1.508
0.068	0.034	0.112	0.055	1.471	0.102	0.027	1.527	0.094	0.023	1.498	0.116	0.030	1.465
0.077	0.031	0.124	0.050	1.441	0.117	0.024	1.493	0.107	0.021	1.460	0.134	0.028	1.430
0.083	0.029	0.132	0.046	1.414	0.131	0.021	1.465	0.118	0.018	1.429	0.151	0.025	1.400
1.000	0.000				1.163	0.000	0.000	1.166	0.000	0.000	1.196	0.000	0.000

ETS-10 zeolite adsorbs ethylene much more strongly in the presence of ethane while the adsorption of these components on SR-115 zeolite is almost equal. Therefore, the separation is much easier on the ETS-10 adsorbent. As mentioned in the Introduction, a recent U.S. patent on the size exclusion of ethane from ethylene employing CTS titanium silicate molecular sieves[2] indicates that this result is not unexpected.

The adsorption behavior of the ternary system methane + ethane + ethylene has been examined in four experiments at two different temperatures 300 K and 325 K and pressure of 200 kPa at different loading of ethylene and ethane. The data obtained at 300 K and 200 kPa (presented in Tables 5 and 6) are compared to the fit of IAST-Toth, IAST-Unilan, and IAST-Virial models at the same conditions. Sample results are tabulated as $x-y$ comparison in Table 5 and $x-q$ comparison in Table 6. The results obtained from the three models are comparable to the data. From consideration of the amount adsorbed at different loading, the concentration of ethane in the adsorbed phase is almost constant at low loading of ethane suggesting that methane molecules replace only ethylene molecules in the adsorbed phase as the partial pressure of methane increases. This conclusion is supported by the three models.

Conclusions

The ideal adsorbed solution theory model (IAST) is used to fit all the multicomponent data obtained on ETS-10 zeolite. The constrained optimized parameters of Toth, Unilan, and Virial three constant isotherms are used in the IAST equations. Similar results have been obtained from the three isotherms. The fit of IAST to the multicomponent systems methane + ethane, ethane + ethylene, methane + ethylene, and methane + ethane + ethylene on ETS-10 zeolite are satisfactory. The fit is best for the alkanes system only and less good for the systems involving ethylene probably due to some nonideality involving this species.

The separation of methane from ethane on ETS-10 zeolite is possible and is better than the separation on 13X and 5A adsorbents (1). The separation of ethane from ethylene is easy on ETS-10 zeolite especially at low temperatures. The effect of pressure on the separation of ethane-ethylene on ETS-10 is not significant.

Acknowledgment

We extend our thanks to S. M. Kuznicki of Engelhard for providing the samples of ETS-10 and to the Research Institute at KFUPM for assistance in extrusion of the ETS-10 samples. The authors acknowledge the support of King Fahd University of Petroleum & Minerals (KFUPM), Dhahran, Saudi Arabia during the course of this work.

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Received for review September 5, 2005. Accepted October 27, 2005.

JE050364C