(16) Stimson, H. F. *J. Res. Natl. Bur. Stand.* **1969**, *73A*, 493.
(17) Osborn, A. G.; Douslin, D. R. *J. Chem. Eng. Data* **1974**, *19*, 114.
(18) Osborn, A. G.; Scott, D. W. *J. Chem. Thermodyn.* **1976**, *10*, 619.
(19) Forziati, A. F.; Norris, W. R.; Rossini, F. D. *J. Res. Natl. Bur. Stand.* **1949**, *43*, 555.
(20) Todd, S. S.; Hossenlopp, I. A.; Scott, D. W. *J. Chem. Thermodyn.* **1978**, *10*, 641.
(21) Douslin, D. R.; McCullough, J. P. *U.S. Bur. Mines* **1963**, *RI 6149*.
(22) Douslin, D. R.; Osborn, A. G. *J. Sci. Instrum.* **1965**, *42*, 369.
(23) Cox, E. R. *Ind. Eng. Chem.* **1936**, *28*, 613.
(24) Scott, D. W.; Finke, H. L.; Gross, M. E.; Guthrie, G. B.; Huffman, H. M. *J. Am. Chem. Soc.* **1950**, *72*, 2424.
(25) Lawrenson, I. J. *NPL Rep. Chem.* (*U.K., Natl. Phys. Lab., Div. Chem. Stand.*) **1977**; *No. 62*.
(26) Tsonopoulos, C. *AIChE J.* **1974**, *20*, 263.
(27) Scott, D. W. *U.S. Bur. Mines Bull.* **1974**, *No. 666*.
(28) Messerly, J. F.; Guthrie, G. B.; Todd, S. S.; Finke, H. L. *J. Chem. Eng. Data* **1967**, *12*, 338.
(29) Osborne, N. S.; Ginnings, D. C. *J. Res. Natl. Bur. Stand.* **1947**, *39*, 453.
(30) Couch, H. T.; Kozicki, W.; Sage, B. H. *J. Chem. Eng. Data* **1963**, *8*, 346.
(31) Goodwin, R. D.; Haynes, W. M. *Thermophysical Properties of Propane from 85 K to 700 K at Pressures to 70 MPa*; NBS Monograph 170; U.S. Department of Commerce: Washington, DC, April 1982.
(32) Goodwin, R. D.; Roder, H. M.; Straty, G. C. *Thermophysical Properties of Ethane, from 90 K to 600 K at Pressures to 700 bar*; NBS Technical Note 684; U.S. Department of Commerce: Washington, DC, August 1976.
(33) Haynes, W. M.; Goodwin, R. D. *Thermophysical Properties of Normal Butane from 135 to 700 K at Pressures to 70 MPa*; NBS Monograph 169; U.S. Department of Commerce, Washington, DC, April 1982.
(34) Kreglewski, A.; Zwolinski, B. J. *J. Phys. Chem.* **1961**, *65*, 1050.
(35) Ambrose, D. *NPL Report Chem.* (*U.K. Natl. Phys. Lab., Div. Chem. Stand.*) **1977**; *No. 67*.

Received for review March 14, 1988. Revised October 17, 1988. Accepted October 25, 1988. The financial support of Exxon Research and Engineering Company is gratefully acknowledged.

Equilibrium Adsorption of Methane, Ethane, Ethylene, and Propylene and Their Mixtures on Activated Carbon

E. Costa, G. Calleja,* C. Marrón, A. Jiménez, and J. Pau

Departamento de Ingeniería Química, Facultad de Ciencias Químicas, Universidad Complutense, 28040 Madrid, Spain

Pure gas adsorption isotherms of methane, ethane, ethylene, and propylene on activated carbon have been determined at 323 K and pressures in the range 0–100 kPa. Binary and ternary adsorption isotherms were also determined at the same temperature and pressures for all the mixtures of these adsorbates, with the exception of methane–propylene mixtures due to their difference in adsorption capacity. Two models have been applied for correlation and prediction of mixture adsorption equilibria—the ideal adsorbed solution (IAS) and the real adsorbed solution (RAS). This second model provides better results for all the systems.

Introduction

Equilibrium adsorption data for mixtures in heterogeneous adsorbents, like activated carbon, are relatively scarce in the literature, existing only a few studies for binary, ternary, and higher order mixtures (*1*–*3*). However, the interest in these mixture equilibria is evident, new accurate data being necessary to validate theoretical models and providing a stronger scientific basis for industrial design.

In a previous paper (*3*) we reported adsorption equilibrium data of light hydrocarbons, methane, ethane, ethylene, and propylene and their mixtures, on a commercial activated carbon, at 293 K. We now present the experimental data corresponding to the same hydrocarbons and their binary and ternary mixtures on the same carbon at a higher temperature, 323 K. All mixtures have been studied, with the exception of binary and ternary mixtures having together methane and propylene, since their adsorption capacity is so different that an uncertain extrapolation of the isotherms would be necessary to calculate spreading pressures of the mixtures.

Among the different models available in the literature for predicting mixture adsorption equilibria (*3*–*8*) we have applied in this study the ideal adsorbed solution (IAS) by Myers and Prausnitz (*4*) and the real adsorbed solution (RAS) previously used by Costa et al. (*3*, *9*), also known as nonideal adsorbed solution.

Experimental Section

***Apparatus*.** The apparatus was of the volumetric type, and was described in detail in previous works (*3*, *10*). Basically it consists of a glass closed circuit with a fixed bed of adsorbent, a membrane compressor for gas circulation, and a volumetric system to introduce and measure the gases admitted, by appropriate P–V–T measurements. The analysis of the gas phase was done by gas chromatography, and the adsorbed phase composition was determined by mass balance from the initial and equilibrium composition of the gas phase. These experiments were performed at 323 K.

***Materials*.** The adsorbent used was a commercial activated carbon, AC-40, from CECA (Comaña Española de Carbón Activo, S.A.), previously used in other adsorption studies (*3*), with a BET surface of 700 m^2/g and a particle porosity of 0.715. The particles had a cylindrical shape of 0.83-mm radius and 4.26-mm height and real and apparent densities of 2700 and 795 kg/m^3, respectively. Regeneration, drying and manipulation conditions of the carbon were the same as described previously (*3*).

Gaseous hydrocarbons used as adsorbates were methane, ethane, ethylene, and propylene, provided by SEO (Sociedad Española de Oxígeno), with a purity higher than 99% in all cases.

Pure-Component Data

The experimental equilibrium isotherms for the pure components methane, ethane, ethylene, and propylene on activated carbon are shown in Table I, at a temperature of 323 K and pressures up to 100 kPa. Curves corresponding to these isotherms are shown in Figure 1, where they can also be compared with the corresponding adsorption isotherms at 293 K,

---

* Author to whom correspondence should be addressed.

0021-9568/89/1734-0156$01.50/0 © 1989 American Chemical Society

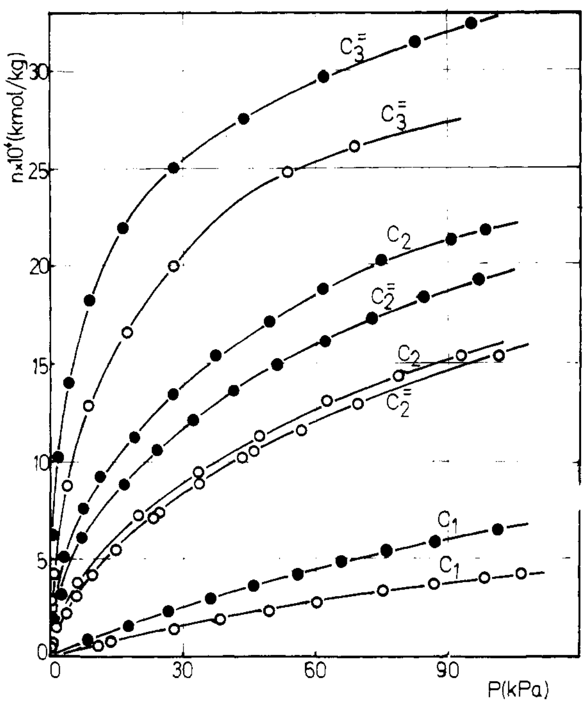

Figure 1. Experimental adsorption isotherms of pure components, methane (C_1), ethane (C_2), ethylene (C_2=), and propylene (C_3=) at 293 (●) and 323 K (○).

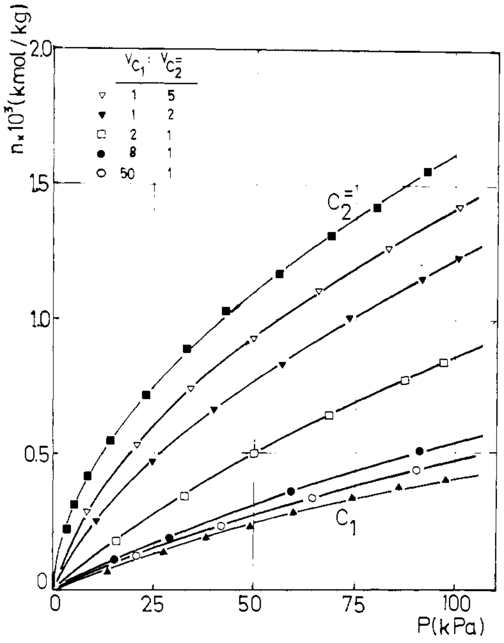

Figure 2. Experimental adsorption isotherms of binary mixtures methane (C_1)-ethylene (C_2=) at 323 K. (▲, pure methane; ■, pure ethylene; other points correspond to binary mixtures of different initial volumetric ratio $V_{C_1}/V_{C_2=}$ as shown).

previously obtained (*3*). The adsorption capacity increases in the order methane-ethylene-ethane-propylene, as shown, and for each adsorbate it decreases for higher temperatures, as expected.

Values of the spreading pressure of the pure components were calculated from the experimental isotherms with the equation

$$\frac{\pi^\circ A}{RT} = \int_0^P \frac{n}{P}\,dP \tag{1}$$

These values are summarized in Table I (column 3) and were used for mixture equilibria calculations.

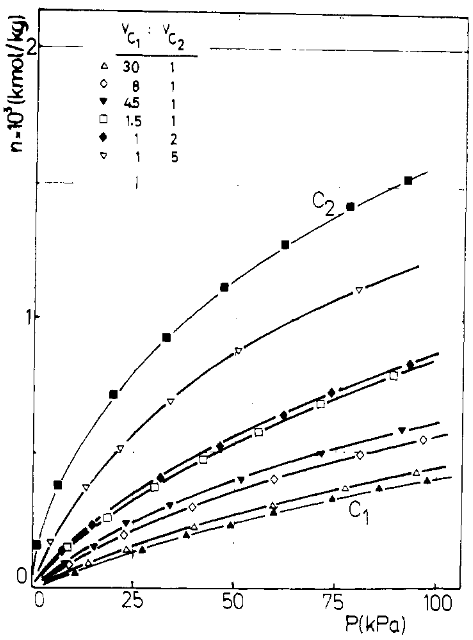

Figure 3. Experimental adsorption isotherms of binary mixtures methane (C_1)-ethane (C_2) at 323 K (▲, pure methane; ■, pure ethane; other points correspond to binary mixtures of different initial volumetric ratio V_{C_1}/V_{C_2}, as shown).

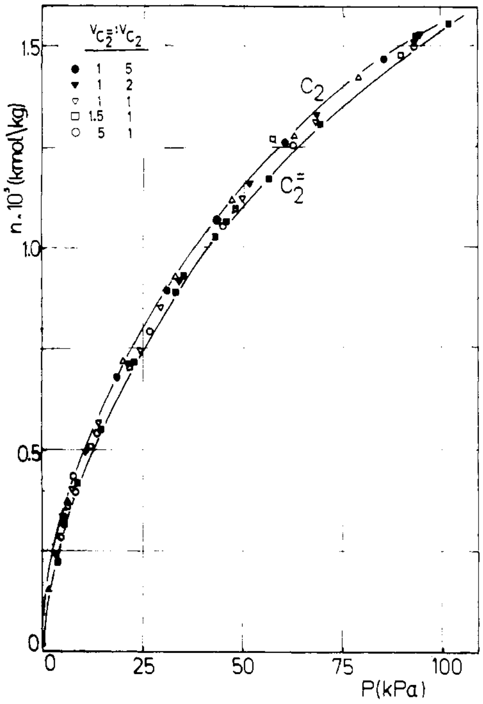

Figure 4. Experimental adsorption isotherms of binary mixtures ethane (C_2)-ethylene (C_2=) at 323 K (△, pure ethane; ■, pure ethylene; other points correspond to binary mixtures of different initial volumetric ratio $V_{C_2=}/V_{C_2}$, as shown).

Binary-Mixture Data

For each binary system, several experimental isotherms were obtained for different initial volumetric ratios, all of them at 323 K and equilibrium pressures up to 100 kPa. Figures 2-6 show the equilibrium isotherms corresponding to the total amounts adsorbed for each binary mixture (5 for methane-ethylene, 6 for methane-ethane, 6 for ethane-ethylene, 7 for ethylene-propylene, and 8 for ethane-propylene).

The curves of each binary mixture lie in the region limited by the two curves of the corresponding pure components, ordered

Table I. Pure Gas Adsorption Data at 323 K

P, kPa	$n \times 10^4$, kmol/kg	$\pi^\circ A/RT \times 10^4$, kmol/kg
	Methane	
10.66	0.573	0.600
13.70	0.761	0.740
27.83	1.429	1.471
38.43	1.958	1.998
49.41	2.336	2.529
60.12	2.819	3.033
75.03	3.380	3.718
86.53	3.750	4.226
98.33	4.083	4.726
106.27	4.285	5.052
	Ethane	
0.36	0.504	1.101
1.40	1.570	3.100
6.45	3.744	6.180
20.33	7.194	11.880
33.53	9.302	15.661
47.51	11.200	18.519
62.75	13.000	20.400
78.66	14.210	22.320
92.94	15.260	23.499
	Ethylene	
0.87	0.746	0.830
3.62	2.246	2.787
5.60	3.154	3.900
9.09	4.212	5.689
14.59	5.482	7.997
23.09	7.172	10.914
24.57	7.460	11.369
33.46	8.916	13.902
43.28	10.290	16.377
45.87	10.642	16.986
56.81	11.690	18.347
69.40	13.054	20.258
101.41	15.500	22.300
	Propylene	
0.33	2.896	3.530
0.80	4.302	8.079
3.78	8.804	17.852
8.61	12.852	26.660
17.41	16.628	36.981
27.90	19.990	45.580
53.62	24.821	60.160
69.77	26.820	66.660

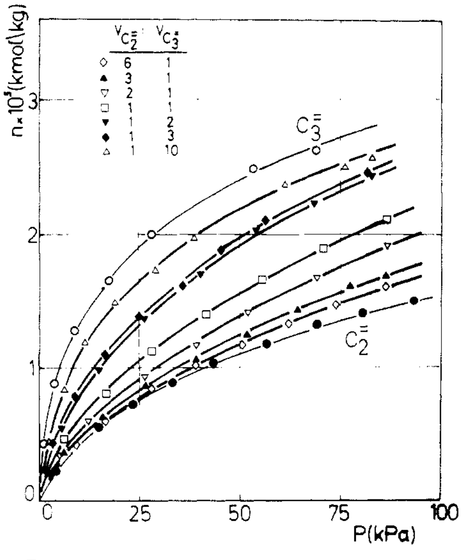

Figure 5. Experimental adsorption isotherms of binary mixtures ethylene (C_2=)-propylene (C_3=) at 323 K. (●, pure ethylene; O, pure propylene; other points correspond to binary mixtures of different initial volumetric ratio $V_{C_2}/V_{C_3=}$, as shown).

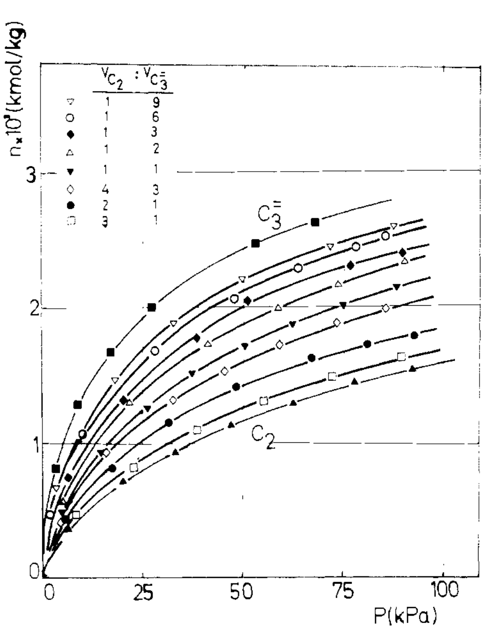

Figure 6. Experimental adsorption isotherms of binary mixtures ethane (C_2)-propylene (C_3=) at 323 K (▲, pure ethane; ■, pure propylene; other points correspond to binary mixtures of different initial volumetric ratio $V_{C_2}/V_{C_3=}$, as shown).

according to their initial volumetric ratio. Only in the case of the system ethylene-ethane the family curves could not be distinguished, due to the proximity of the isotherms of the pure components (Figure 4). This adsorption capacity, similar for both hydrocarbons, shows that the presence of a double bond in the adsorbate molecule does not necessarily mean a different behavior in the adsorption process; that is, no additional significant adsorption interactions appear as a consequence of the double bond, with a higher electronic density. This was not the case, however, in the adsorption of the same hydrocarbons on 5A zeolite, where ethane and ethylene showed rather different adsorption capacities. This difference in behavior is obviously a result of the difference of structure and properties of both types of adsorbents.

From the experimental isotherms of binary mixtures, at a given equilibrium total pressure, interpolation in each curve allows calculation of the molar fractions of adsorbed and gaseous phases, so that the isobaric adsorption equilibrium diagram can be obtained for each binary system. Thus, y-x adsorption phase diagrams were determined at 10 kPa for all binary systems, as shown in Table II, which also includes the total amount adsorbed, n, for the same total pressure, and the corresponding activity coefficients in the adsorbed phase, calculated as commented later.

Prediction of the adsorption equilibrium of the five binary systems with the ideal adsorption solution (IAS) (*4*) is based on Raoult's equation:

$$Py_i = P_i^\circ(\pi)x_i \qquad (2)$$

The modification of this model by introducing an activity coefficient of component i in the adsorbed phase, γ_i, in Raoult's law leads to the so-called real adsorption solution (RAS) (*3*, *9*, *11*), so that eq 2 becomes

$$Py_i = P_i^\circ(\pi)x_i\gamma_i \qquad (3)$$

This model needs a new equation to calculate the activity coefficients, which depends on the composition of the adsorbed phase. As in a previous work (*3*), we have used the Wilson equation (*12*), well-known in vapor-liquid equilibrium, which has

Table II. Binary Gas Mixture Adsorption Data at 323 K and 10 kPa

x_1	y_1	$n \times 10^4$, kmol/kg	γ_1	γ_2
Methane (1)-Ethylene (2)				
$\Lambda_{12} = 1.100$; $\Lambda_{21} = 1.100$				
0.052	0.423	3.150	0.910	0.990
0.123	0.664	2.331	0.902	0.980
0.364	0.908	1.204	0.959	0.928
0.688	0.978	0.743	0.975	0.872
0.889	0.994	0.658	0.980	0.811
Methane (1)-Ethane (2)				
$\Lambda_{12} = 1.178$; $\Lambda_{21} = 1.100$				
0.030	0.371	2.980	0.770	0.993
0.110	0.769	1.725	0.820	0.984
0.235	0.923	1.625	0.911	0.979
0.465	0.975	1.050	0.950	0.950
0.673	0.990	0.925	0.972	0.886
0.860	0.998	0.610	0.990	0.780
Ethylene (1)-Ethane (2)				
$\Lambda_{12} = 1.000$; $\Lambda_{21} = 1.000$				
0.122	0.164	4.925	0.997	1.003
0.321	0.400	4.731	0.985	1.020
0.450	0.555	4.700	1.004	1.011
0.594	0.690	4.569	1.011	1.021
0.734	0.805	4.500	1.013	1.054
Ethylene (1)-Propylene (2)				
$\Lambda_{12} = 1.100$; $\Lambda_{21} = 1.419$				
0.045	0.348	11.250	0.674	0.982
0.145	0.657	8.551	0.758	0.955
0.203	0.750	7.848	0.810	0.926
0.342	0.894	6.150	0.871	0.848
0.532	0.957	5.400	0.905	0.774
0.632	0.976	4.901	0.930	0.730
0.775	0.989	4.498	0.958	0.679
Ethane (1)-Propylene (2)				
$\Lambda_{12} = 1.352$; $\Lambda_{21} = 1.635$				
0.058	0.274	11.009	0.412	0.998
0.083	0.405	10.840	0.500	0.969
0.156	0.595	9.201	0.580	0.942
0.225	0.693	8.399	0.610	0.931
0.382	0.846	7.250	0.701	0.871
0.452	0.906	7.050	0.775	0.771
0.551	0.939	5.902	0.794	0.738
0.846	0.992	5.110	0.966	0.536

only binary mixture parameters, even for multicomponent mixtures:

$$\ln \gamma_i = 1 - \ln \left(\sum_j x_j \Lambda_{ij}\right) - \sum_k \frac{x_k \Lambda_{ki}}{\sum_j x_j \Lambda_{kj}} \qquad (4)$$

Equations 3 and 4 permit estimation of equilibrium for binary mixtures, once the parameters Λ_{ij} have been calculated from the experimental data, and therefore allow prediction of ternary and higher equilibrium data with no additional mixture parameters. The calculation procedure for reproducing and predicting the adsorption equilibria were presented previously (*3*, *11*).

Following this procedure, activity coefficients were calculated for each adsorbate from the experimental binary data, which are shown in Table II. Binary constants of Wilson's equation, Λ_{12} and Λ_{21}, are also included in Table II. It is observed, from this data, that the binary system ethane-ethylene shows the closest behavior to ideality, with γ_i practically equal to unity for all compositions (values higher than 1.0 are within the experimental error). On the other hand, ethane-propylene and ethylene-propylene mixtures show the largest deviations from ideality. These results are in agreement with our previous work with the same systems, at a lower temperature of 293 K (*3*). As an example, Figures 7 and 8 show the adsorption equilibrium diagrams of the systems ethylene-ethane and ethane-propylene, respectively, at 323 K and 10 kPa. It is observed that the ethylene-ethane system is well predicted by the IAS model, due to its ideal behavior, whereas this model does not give satisfactory results with the ethane-propylene system, which deviates from ideality. The RAS model, however, gives very good results in both cases, providing a useful tool particularly for those systems showing a clear nonideal behavior.

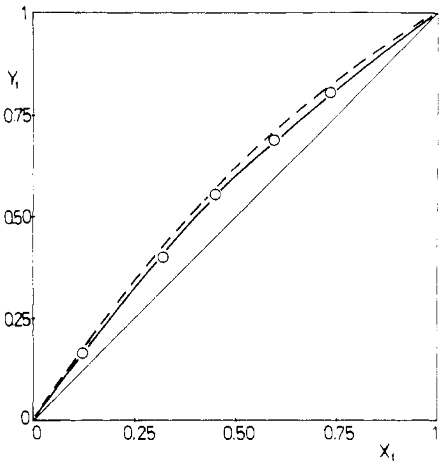

Figure 7. Experimental and calculated equilibrium data of binary mixture ethylene (1)-ethane (2) at 323 K and 10 kPa (O, experimental; --, IAS; —, RAS).

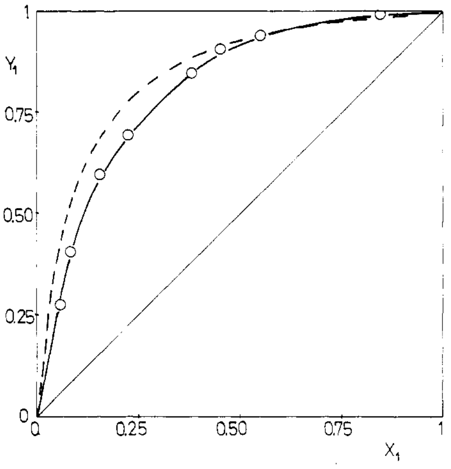

Figure 8. Experimental and calculated equilibrium data of binary mixture ethane (1)-propylene (2) at 323 K and 10 kPa (O, experimental; --, IAS; —, RAS).

Ternary-Mixture Data

Five adsorption isotherms were experimentally obtained for the ternary system methane-ethylene-ethane and seven for the system ethylene-ethane-propylene, each one for a given initial volumetric ratio of hydrocarbons, at a temperature of 323 K and pressures up to 100 kPa.

Following a procedure similar to that for binary mixtures, the isobaric equilibrium data were obtained for the two ternary systems, in terms of molar fractions in the adsorbed phase (x_i) and in the gas phase (y_i). Table III shows these data at a pressure of 10 kPa, and 323 K and the values of y_i predicted from IAS and RAS models for each value of x_i, with the corresponding deviation errors with respect to the experimental values.

For both models, Table III also shows values of the activity coefficients in the adsorbed phase, obtained from Wilson's equation for ternary mixtures by using the binary constants Λ_{ij} presented in Table II. It is observed that the introduction of the activity coefficients in Raoult's law allows a much better prediction of the equilibria, showing the deviation from ideality

Table III. Ternary Gas Mixture Adsorption Data and Prediction Results at 323 K and 10 kPa Total Pressure

	experimental		IAS		RAS		
comp	x_{exptl}	y_{exptl}	y_{calcd}	e, %	y_{calcd}	e, %	γ_{calcd}
	Methane (1)–Ethylene (2)–Ethane (3)						
1	0.325	0.920	0.919	0.05	0.913	0.76	0.899
2	0.333	0.052	0.060	16.15	0.064	23.08	0.988
3	0.342	0.029	0.020	31.03	0.022	24.14	0.965
1	0.192	0.841	0.862	2.55	0.842	0.12	0.853
2	0.278	0.069	0.083	19.56	0.094	36.23	0.998
3	0.530	0.090	0.055	39.11	0.062	31.11	0.987
1	0.197	0.815	0.828	1.64	0.809	0.74	0.867
2	0.520	0.151	0.145	4.17	0.162	7.28	0.996
3	0.283	0.034	0.027	21.18	0.031	8.82	0.983
1	0.127	0.682	0.738	8.21	0.700	2.77	0.845
2	0.570	0.264	0.217	17.92	0.250	5.30	0.999
3	0.303	0.054	0.045	16.30	0.050	7.41	0.991
1	0.046	0.490	0.477	2.71	0.471	3.88	0.801
2	0.457	0.340	0.343	0.85	0.335	1.47	0.997
3	0.497	0.170	0.180	6.00	0.193	13.53	0.979
	Ethylene (1)–Ethane (2)–Propylene (3)						
1	0.382	0.580	0.548	5.43	0.565	2.59	0.999
2	0.438	0.407	0.439	7.49	0.424	4.18	0.948
3	0.180	0.013	0.014	7.69	0.011	15.30	0.632
1	0.177	0.315	0.292	7.36	0.310	1.59	0.999
2	0.597	0.665	0.686	3.21	0.664	0.15	0.937
3	0.244	0.020	0.022	9.00	0.016	20.00	0.640
1	0.541	0.791	0.777	1.73	0.795	0.50	0.994
2	0.203	0.187	0.203	8.45	0.190	1.60	0.898
3	0.255	0.018	0.020	10.00	0.015	16.67	0.723
1	0.447	0.730	0.702	3.89	0.735	0.68	0.989
2	0.244	0.247	0.272	10.16	0.245	0.81	0.875
3	0.309	0.023	0.026	13.91	0.020	13.04	0.741
1	0.286	0.564	0.534	5.34	0.572	1.42	0.977
2	0.307	0.390	0.424	8.64	0.388	0.57	0.831
3	0.408	0.045	0.042	6.00	0.040	11.11	0.779
1	0.215	0.390	0.371	4.77	0.401	2.82	0.999
2	0.476	0.584	0.599	2.59	0.575	1.54	0.900
3	0.310	0.023	0.029	27.39	0.023	0.00	0.695
1	0.619	0.840	0.831	1.05	0.838	0.24	0.996
2	0.171	0.147	0.153	4.29	0.150	2.04	0.916
3	0.210	0.012	0.015	27.50	0.011	8.33	0.705

of the adsorbed mixtures. Higher deviation errors for the RAS model only appear for component 3 for very low molar fractions (Table III), but they are less significant, since they represent relative deviations, as the absolute deviations were always very small and within the experimental error.

Finally, the average mean deviation was calculated, as a parameter representing the average deviation of the two prediction models for the ternary mixtures:

$$\sigma_y = \left[\frac{(y_{\text{exptl}} - y_{\text{calcd}})^2}{N - 1} \right]^{1/2} \qquad (5)$$

Values obtained for this parameter are the following:

ternary system	σ_y (IAS)	σ_y (RAS)
$C_1/C_2{=}/C_2$	0.0240	0.0139
$C_2{=}/C_2/C_3{=}$	0.0923	0.0307

showing again that the RAS model provides a more useful method for prediction of mixture adsorption equilibria than the IAS model.

Glossary

A	total area of adsorbate, m^2
e	deviation error, relative difference between calculated and predicted values
n	total amount adsorbed, kmol of adsorbate/kg of adsorbent
P	equilibrium pressure, kPa
$P_i{}^{\circ}(\pi)$	equilibrium pressure for pure component i, corresponding to spreading pressure π, kPa
R	gas constant, m^3·kPa/(kmol·K)
T	absolute temperature, K
x_i	molar fraction of component i in the adsorbed phase
y_i	molar fraction of component i in the gas phase

Greek Letters

γ_i	activity coefficient of component i in the adsorbed phase
Λ_{ij}	Wilson's binary constant parameters
π	spreading pressure of the mixture
π°	spreading pressure of the pure component
σ_y	mean deviation (eq 5)

Registry No. C, 7440-44-0; methane, 74-82-8; ethane, 74-84-0; ethylene, 74-85-1; propylene, 115-07-1.

Literature Cited

(1) Tsai, M. C.; Chen, W. N.; Cen, P. L.; Yang, R. T. *Carbon* **1985**, *24*, 2.
(2) Wilson, R. J.; Danner, R. P. *J. Chem. Eng. Data* **1983**, *28*, 14.
(3) Costa, E.; Sotelo, J. L.; Calleja, G.; Marrón, C. *AIChE J.* **1981**, *27*, 5.
(4) Myers, A. L.; Prausnitz, J. M. *AIChE J.* **1965**, *11*, 121.
(5) Ruthven, D. M. *Principles of Adsorption and Adsorption Processes*; Wiley: New York, 1984.
(6) Cochran, W.; Kabel, R. L.; Danner, R. P. *AIChE J.* **1985**, *31*, 268.
(7) O'Brien, J. A.; Myers, A. L. *Ind. Eng. Chem. Process Des. Dev.* **1985**, *24*, 1188.
(8) Talu, O.; Zwiebel, I. *AIChE J.* **1986**, *32*, 1263.
(9) Costa, E.; Calleja, G.; Cabra, L. *R. Acad. Cienc. Exactas Fis. Nat. Madrid* **1982**, *76*(4), 908.
(10) Costa, E.; Calleja, G.; Cabra, L. *Adsorpt. Sci. Technol.* **1984**, *1*, 307.
(11) Costa, E.; Calleja, G.; Cabra, L. *Fundamentals of Adsorption*; Myers, A. L., Belfort, G., Eds.; Engineering Foundation: New York, 1984.
(12) Wilson, G. M. *J. Am. Chem. Soc.* **1964**, *86*, 127.

Received for review May 24, 1988. Accepted November 2, 1988.