Adsorption Of Binary And Ternary Hydrocarbon Gas Mixtures On Activated Carbon: Experimental Determination And Theoretical Prediction Of The Ternary Equilibrium Data

Experimental binary and ternary equilibrium data for the adsorption of hydrocarbon mixtures of methane, ethane, ethylene, and propylene on activated carbon at 20°C are presented and discussed. Reproduction of binary adsorption equilibria and prediction of ternary adsorption equilibria exclusively with data of binary systems have been carried out using a real adsorbed solution theory, which requires the calculation of the activity coefficients for the components in the adsorbed phase.

Predicted equilibrium data are found to be in excellent agreement with experimental values using Wilson and UNIQUAC equations to calculate the activity coefficients. The real absorbed solution theory provides a much more accurate method for predicting multicomponent adsorption equilibria than the ideal adsorbed solution theory.

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SCOPE

The use of adsorption for the separation of gas mixtures has been continuously increasing. The main advantages of adsorption as compared with other separation techniques are the high selectivity that can be attained and the relatively high capacity of the adsorbents for volatile compounds, even at low partial pressures. Some applications of interest include the purification of methane, ethylene, and other light hydrocarbons; the covery of LPG from natural and refinery gas streams; the separation of olefins from cracked gases; and the recovery of acetylene and other pretrochemicals from dilute mixtures with other hydrocarbon gases.

Although there are a great deal of publications on adsorption of mixtures of hydrocarbons on porous solids (Hill, 1949; Young and Crowell, 1962; Myers and Prausnitz, 1965; Van Ness, 1969; Eberly, 1971; Veyssière and Cointot, 1975; Ruthven, 1973, Danner and Choi, 1978), only a limited amount of basic equilibrium data for the design of commercial activated carbon-based separation systems has been published (Myers, 1965; Szepesy and Illés, 1963; Friederich and Mullins, 1972).

On the other hand, most of the theoretical work based on the analogy between the thermodynamics of solutions and the thermodynamics of mixed adsorbates predicts adsorption equilibria using the assumption of an ideal behavior of the adsorbates on the solid surface, which can be expressed in terms of a Raoult's type law (Myers, 1965). However, predicted adsorption equilibria are not always found to be in good agreement with experimental data. Certainly, there is a competition of the adsorbed molecules for the active centers of the solid surface, due to the different adsorption capacity of the adsorbates, so that the ideal adsorbed solution theory can be improved modifying the Raoult's law by the introduction of the activity coefficients for the components in the adsorbed phase.

This paper discusses new experimental data on adsorption for binary and ternary hydrocarbon mixtures on activated carbon at 20°C and a total pressure up to 760 mm Hg (101.33 K Pa). A thermodynamic method based on a real adsorbed solution theory is applied to reproduce experimental binary adsorption equilibria and to predict ternary adsorption equilibria, only with binary systems data, calculating the activity coefficients for the components in the adsorbed phase by means of Wilson and UNIQUAC equations for vapor-liquid equilibrium.

CONCLUSIONS AND SIGNIFICANCE

An experimental technique based on a fluidized adsorbent bed can be used to determine adsorption equilibria of gaseous mixtures in porous solids, which are fundamental to the design of adsorption separation systems.

Experimental adsorption isotherms of binary and ternary mixtures of methane, ethylene, ethane and propylene on activated carbon were obtained at 20 and 50°C and absolute pressures in the range 0-750 mm Hg, using gas chromatography for the analysis of the gaseous phase. Small variations of the equilibrium diagrams y-x with total pressure have been noticed, as in vapor-liquid equilibria. To have more accurate

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prediction techniques of multicomponent adsorption equilibria, a thermodynamic method has been applied to reproduce experimental binary and ternary adsorption equilibria. This method is based on the analogy between the thermodynamics of solutions and the thermodynamics of absorbed mixtures, using a real adsorbed solution theory.

Using Wilson and UNIQUAC equations to calculate the activity coefficients of the components in the adsorbed phase, we found that experimental and predicted data are in excellent agreement. These activity coefficients, that account for the interaction between the adsorbates on the adsorbent surface, appear to vary with composition in a similar form to that corresponding to typical vapor-liquid equilibria of mixtures not very different from ideality, and the values calculated are in the range 1-0.5. Values closer to unity correspond to mixtures closer to ideality, as ethane-ethylene. This confirms again the analogy between the thermodynamics of solutions and the thermodynamics of adsorbed mixtures.

The agreement between predicted and experimental data seems to be much better than that corresponding to the ideal adsorbed solution theory, for which activity coefficients in the adsorbed phase are assumed to be unity. One of the main advantages of using Wilson and UNIQUAC equations, as in the case of the vapor-liquid equilibrium, is the ability to predict activity coefficients of ternary or multicomponent adsorbed mixtures from experimental data of binary mixtures only.

THEORY

Hill (1949), Myers and Prausnitz (1965), and Van Ness (1969) developed a thermodynamic treatment of the gas adsorption equilibria based on the obvious analogy between vapor-liquid and gas-adsorbate systems.

During the adsorption phenomena, the properties of the fluid and solid phases change in the neighborhood of the interfacial surface forming an ill-defined interfacial region. According to the original idea of Gibbs, this difficulty is circumvented by replacing the actual system of the two above-metioned phases and a condensed two-dimensional phase, with another hypothetical integrated for the fluid phase with its own thermodynamic properties. This condensed phase partially covers the adsorbent surface that will be assumed uninfluenced by temperature, pressure, composition, or amount of adsorbate.

Pressure and Superficial Area

The global closed system consists of two open subsystems: a three-dimensional gas phase (g) and a two-dimensional adsorbate phase (a). Considering this system, the differential variation of the Gibbs's free energy for both of them will be:

$$dG^g = -S^g dT + V^g dp + \sum_{i=1}^{c} \mu_i^g dN_i^g \tag{1}$$

for the first one, and

$$dG^a = -S^a dT + A^a d\pi + \sum_{i=1}^{c} \mu_i^a dN_i^a \tag{2}$$

for the second one. Π and A are respectively the spreading pressure and the total surface of the adsorbent, replacing the pressure p and the volume V for the gas phase in Eq. 1.

Considering the expression of the Gibbs's free energy G, as a function of the chemical potential μ_i, assuming an ideal behavior of the gas phase and expressing the chemical potential μ_i as a function of its composition y_i by basic thermodynamics, keeping in mind the equilibrium condition, Eq. 3 ($\mu_i^g = \mu_i^a$), Eq. 2 gives:

$$-\frac{A}{RT} d\Pi + N_t \, d\ln p + \sum_{i=1}^{c} N_i d\ln y_i = 0 \; (T = \text{const.}) \tag{3}$$

Integrating this equation for a pure component (constant gas composition) between the limits $p=0$, $\Pi=0$, and $p=p$, $\Pi=\Pi$ gives the following expression:

$$\frac{\Pi_i^0 A}{RT} = \int_0^p \frac{N_t}{p} dp \tag{4}$$

Eq. 4 provides the means to calculate the spreading pressure of each component (Π_i^0), needed to estimate the spreading pressure of the mixture (Π), using the information from the experimental adsorption isotherms (N_t vs. p) of the pure components.

If we now consider a binary system of components 1 and 2, Eq. 3 integrated between limits: $y_1 = 1$, $\Pi = \Pi_1^0$ and $y_1 = y_1$, $\Pi = \Pi$ gives:

$$\frac{A}{RT} \Delta\Pi = \int_1^{y_1} N_t \frac{x_1 - y_1}{y_1(1-y_1)} dy_1 \quad (\text{P,T=const.}) \tag{5}$$

where

$$\Delta\Pi = \Pi - \Pi_1^0 \therefore \Pi = \Pi_1^0 + \Delta\Pi \tag{6}$$

Eqs. 5 and 6 can be used to calculate the spreading pressure of any binary mixtures (Π), being its value always comprised between the spreading pressures Π_1^0 and Π_2^0 of the less and more adsorbed pure components respectively.

Real Behavior of the Adsorbate: Modified Raoult's Law

The prediction of gas-solid adsorption equilibria may be followed by two different approaches, according to the assumed behavior (ideal or real) of the adsorbed phase. The first approach assumes that each of the adsorbates in the adsorbed phase behaves independently of the presence of the molecules of the other adsorbates. In the second approach, the possible interactions between the molecules of the different adsorbates competing to occupy the active centers of the adsorbent surface are considered.

Accounting for the real behavior of the molecules of the adsorbate requires the calculation of the activity coefficients of the components. Myers and Prausnitz (1965), applying basic thermodynamic relationships to the adsorbed phase, developed an expression for the chemical potential of the components as a function of the mixture composition and the activity coefficients. At the equilibrium, equating the chemical potentials of each component in both phases, the following expression was obtained:

$$p \, y_i = \gamma_i \, p^0{}_i(\Pi) \, x_i \tag{7}$$

This expression can be regarded as a modified form of Raoult's law for vapor-liquid systems, with the vapor pressure of pure components at the equilibrium temperature replaced by the pressure p_i^0 (Π). This new term p_i^0 (Π) can be physically interpreted as the pressure that the pure component i should have in the gas phase to give rise, when adsorbed, to the same spreading pressure Π of the mixture at the same temperature.

The necessary values of the pressure p_i^0 (Π) in Eq. 7 can be obtained from a plot of $\Pi_i^0 A/RT$ vs. p (for pure components), being the abscissa corresponding to $\Pi A/RT$ of the mixture given by Eq. 6.

In the case of an ideal binary mixture, although the equilibrium data could be calculated directly from the isotherms of the two pure components, it would be also possible to use Raoult's law (Eq. 7) with $\gamma_1 = \gamma_2 = 1$ to calculate the pressures p_i^0 (Π) as indicated before. This method was previously used by Myers and Prausnitz (1965).

Prediction of Adsorption Equilibria

Young and Crowell (1962) have summarized the existing methods used until 1962 to predict the adsorption equilibria. Most of them are based on Langmuir and B.E.T. equations for fixed beds.

Later, Myers (1965) developed a model to predict the adsorption equilibria of binary mixtures from the adsorption isotherms of the pure components, assuming an ideal behavior of the adsorbate ($\gamma_1 = \gamma_2 = 1$). Reproduction of the experimental data of Szepesy and Illés (1963) with their model was not very successful. More recently, Friederich and Mullins (1972), using a Van der Waals-type state equation for the adsorbed phase, proposed a new model that yields results in good agreement with Myers.

In any case, up to now, methods for prediction of adsorption equilibria based on the analogy with vapor-liquid equilibria have assumed ideal behavior of the adsorbed phase. This hypothesis is only valid for mixtures of components with similar adsorption capacities. Therefore, these methods show more appreciable deviations for mixtures with components of different adsorption capacities, specially in the high dilution ranges, as in the case of the purification processes of some light hydrocarbons (methane, ethane, etc).

Considering the parallelism between the thermodynamics of solutions and the thermodynamics of the actual adsorbed phases ($S^E \neq 0$; $H^E \neq 0$), it seems reasonable to use Wilson (1964) and UNIQUAC (1975) equations to determine the activity coefficients of the adsorbed components, assuming as a first approximation that the physical meaning of the parameters of such equation is still valid for the adsorbed phase.

The expression of the well-known Wilson equation for the activity coefficients of a liquid-mixture component is:

$$\ln \gamma_i = -\ln\left(1 - \sum_{i=1}^{c} x_j \Lambda_{ji}\right) + 1 - \frac{\sum_{j=1}^{c} x_j (1 - \Lambda_{ij})}{1 - \sum_{k=1}^{c} x_k \Lambda_{kj}} \tag{8}$$

where the binary constants Λ_{ij} Λ_{ji}, Λ_{kj}, must be experimentally determined.

With the UNIQUAC equation developed by Abrams and Prausnitz, it is possible to calculate the activity coefficients of the liquid mixture components knowing the structural parameters s_i and r_i and the coordination index, z, of the individual molecules, reported by Bondi (1968). This equation can be written as:

$$\ln \gamma_i = \ln \frac{\phi_i}{x_i} + \frac{z}{2} s_i \ln \frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i} \sum_j x_j l_j + s_i \left[1 - \ln\left(\sum_j \theta_j \tau_{ji}\right) - \sum_j \frac{\theta_i \tau_{ij}}{\sum_k \theta_k \tau_{kj}}\right] \tag{9}$$

with

$$\theta_i = \frac{s_i x_i}{\sum_j s_j x_j}; \quad \phi_i = \frac{r_i x_i}{\sum_j r_j x_j};$$

$$l_j = \frac{z}{2}(r_j - s_j) - (r_j - 1) \tag{10}$$

where the binary constants τ_{ij} and τ_{ji} must be experimentally determined.

Both equations (Wilson and UNIQUAC) have empirical constants of only binary mixtures, being therefore very useful for predicting activity coefficients in multicomponent mixtures without further experimental data required. We use both of them, in the present work, to predict the adsorption equilibria of multicomponent gas mixtures.

EXPERIMENTAL SYSTEM

The equipment was built of pyrex glass and constituted of the following fundamental elements: a fluidized bed of adsorbent; an oil-free compressor for circulating the mixture; and a gas chromatograph for the analysis of the gas mixture. The three of them were arranged in a closed circuit, Figure 1. The bed was provided with a jacket to maintain a constant temperature during the adsorption runs and the adsorbent regenerations.

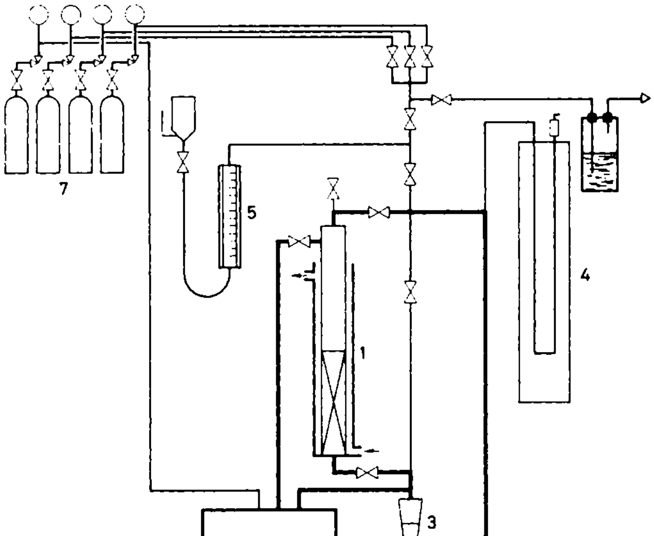
The characteristics of the adsorbent and gases used were:

- Activated carbon type AC-40, supplied by Compañia Españo la de Carbones Activos S.A., with a B.E.T. surface area of 700 m^2/g, particle porosity of 0.715, cylindrical with 0.83-mm radius and 4.26-mm height, real density of 2.70 g/cm^3, and apparent density of 0.795 g/cm^3.
- Hydrocarbon gases supplied by Sociedad Española de Oxigeno S.A.: methane (99,95% min.), ethane (99% min.), ethylene (99,93% min.) and propylene (99% min.).

A known amount of adsorbent (50 g of activated carbon) was introduced in the reactor and degasified by heating up to 270°C and reducing the pressure to 0.1 mm Hg. These conditions were maintained in the installation for a period of at least 12 hours. Then, the dilutant gas (helium) was introduced to the system until an absolute pressure of 200 mm Hg was reached. Finally, successive amounts of the hydrocarbons were added until a total pressure of 750 mm Hg was attained.

The experimental data points of the adsorption isotherms are obtained by: 1. introducing successive known volumes of adsorbate in the circuit; and 2. homogenizing the gaseous mixture by recirculating it through the by-pass. Then, the mixture is made to flow repeatedly through the adsorbent bed until the steady state, characteristic of the equilibrium, is attained. This is observed by periodic analysis of 0.1 cm^3 gaseous samples. The amount of adsorbed phase is calculated by material balance.

Experiments were carried out at 20 and 50°C and the absolute pressure of equilibrium of the adsorbates were in the range 0-750 mm Hg. In such conditions, the adsorption of helium was negligible.



1 ADSORPTION BED
2 COMPRESSOR
3 FLOW METER
4 MANOMETER
5 GAS BURET
6 CHROMATOGRAPH & RECORDER
7 HYDROCARBONS & He SOURCES

Figure 1. Experimental system.

TABLE 1. EXPERIMENTAL EQUILIBRIUM DATA AND SPREADING PRESSURE FOR THE PURE COMPONENTS

Methane			Ethylene		
N_t (gmol)	p (mm Hg)	$\frac{\Pi^\circ A}{RT}$	N_t (gmol)	p (mm Hg)	$\frac{\Pi^\circ A}{RT}$
$4.206\ 10^{-3}$	63.27	$4.714\ 10^{-3}$	$6.500\ 10^{-3}$	4.10	$6.010\ 10^{-3}$
$7.909\ 10^{-3}$	131.70	$9.043\ 10^{-3}$	$1.592\ 10^{-2}$	17.99	$2.471\ 10^{-2}$
$1.169\ 10^{-2}$	199.12	$1.305\ 10^{-2}$	$3.029\ 10^{-2}$	52.09	$4.847\ 10^{-2}$
$1.484\ 10^{-2}$	272.95	$1.722\ 10^{-2}$	$4.399\ 10^{-2}$	125.00	$8.217\ 10^{-2}$
$1.823\ 10^{-2}$	344.53	$2.106\ 10^{-2}$	$5.252\ 10^{-2}$	181.44	$1.005\ 10^{-1}$
$2.121\ 10^{-2}$	420.05	$2.497\ 10^{-2}$	$6.056\ 10^{-2}$	242.32	$1.169\ 10^{-1}$
$2.425\ 10^{-2}$	495.14	$2.870\ 10^{-2}$	$6.796\ 10^{-2}$	309.34	$1.326\ 10^{-1}$
$2.712\ 10^{-2}$	571.83	$3.240\ 10^{-2}$	$7.459\ 10^{-2}$	384.10	$1.481\ 10^{-1}$
$2.947\ 10^{-2}$	653.87	$3.619\ 10^{-2}$	$8.060\ 10^{-2}$	465.00	$1.630\ 10^{-1}$
$2.282\ 10^{-2}$	761.09	$4.092\ 10^{-2}$	$8.659\ 10^{-2}$	546.12	$1.764\ 10^{-1}$
Ethane			$9.209\ 10^{-2}$	632.00	$1.895\ 10^{-1}$
$5.900\ 10^{-3}$	1.80	$8.186\ 10^{-3}$	$9.658\ 10^{-2}$	728.00	$2.002\ 10^{-1}$
$1.009\ 10^{-2}$	4.75	$1.821\ 10^{-2}$	Propylene		
$2.564\ 10^{-2}$	25.67	$4.534\ 10^{-2}$	$1.390\ 10^{-2}$	0.24	$1.166\ 10^{-2}$
$3.800\ 10^{-2}$	56.13	$7.169\ 10^{-2}$	$3.105\ 10^{-2}$	2.56	$3.366\ 10^{-2}$
$4.608\ 10^{-2}$	85.38	$8.938\ 10^{-2}$	$5.090\ 10^{-2}$	12.80	$1.161\ 10^{-1}$
$5.597\ 10^{-2}$	143.14	$1.151\ 10^{-1}$	$7.005\ 10^{-2}$	30.03	$1.705\ 10^{-1}$
$6.700\ 10^{-2}$	208.42	$1.382\ 10^{-1}$	$9.095\ 10^{-2}$	64.90	$2.356\ 10^{-1}$
$7.708\ 10^{-2}$	282.90	$1.601\ 10^{-1}$	$1.095\ 10^{-1}$	122.19	$3.014\ 10^{-1}$
$8.539\ 10^{-2}$	374.80	$1.820\ 10^{-1}$	$1.252\ 10^{-1}$	209.14	$3.666\ 10^{-1}$
$9.401\ 10^{-2}$	463.74	$2.001\ 10^{-1}$	$1.377\ 10^{-1}$	327.70	$4.268\ 10^{-1}$
$1.015\ 10^{-1}$	564.04	$2.172\ 10^{-1}$	$1.486\ 10^{-1}$	463.78	$4.773\ 10^{-1}$
$1.073\ 10^{-1}$	680.93	$2.318\ 10^{-1}$	$1.575\ 10^{-1}$	618.47	$5.217\ 10^{-1}$
$1.087\ 10^{-1}$	737.32	$2.350\ 10^{-1}$	$1.620\ 10^{-1}$	713.63	$5.447\ 10^{-1}$

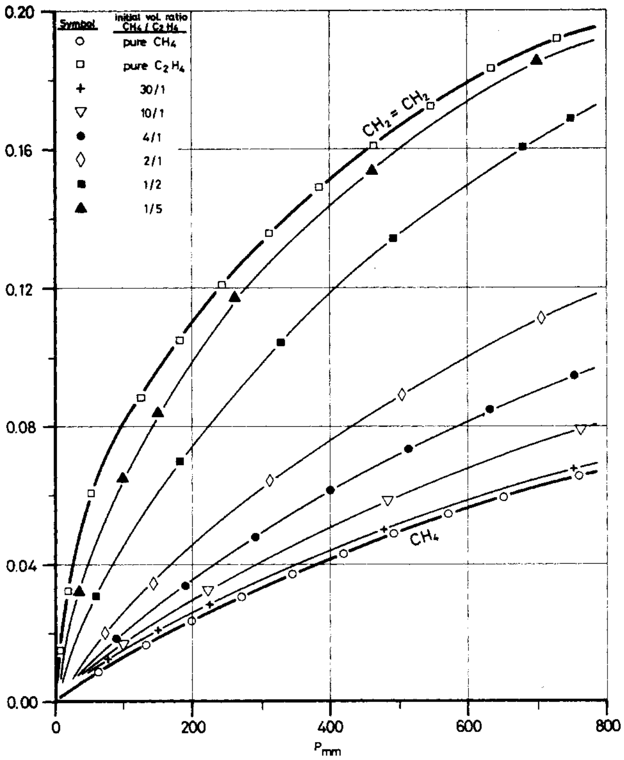


Figure 2. Equilibrium isotherms of CH_4 and C_2H_4 mixtures at 20°C.

RESULTS AND DISCUSSION

Adsorption isotherms in the range 0-750 mm Hg pressure and 20-50°C temperature have been obtained for the following cases:

Pure Components: methane, ethylene, ethane and propylene.

Binary Mixtures: methane-ethylene, methane-ethane, ethylene-ethane, ethylene-propylene and ethane-propylene.

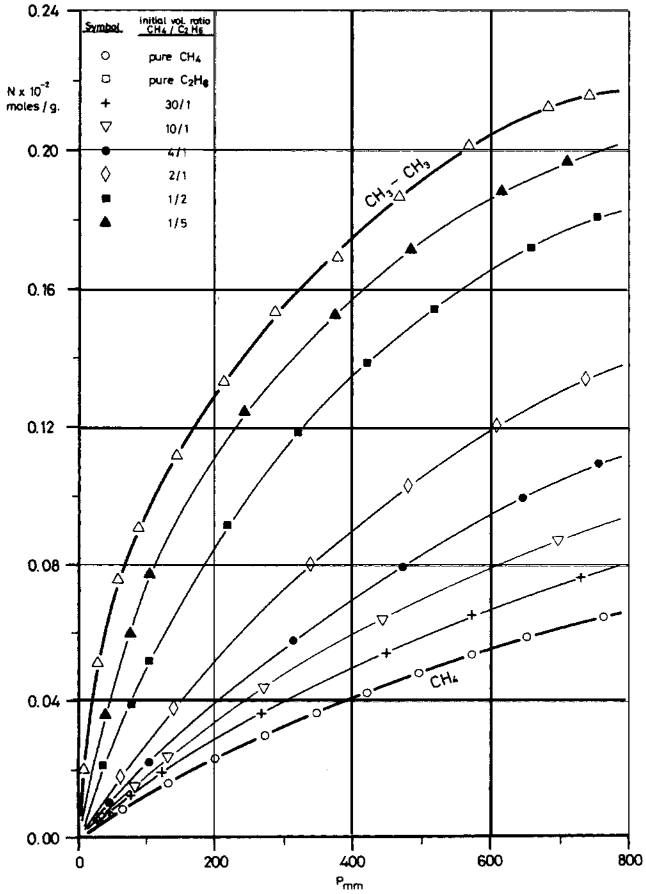


Figure 3. Equilibrium isotherms of CH_4 and C_2H_6 mixtures at 20°C.

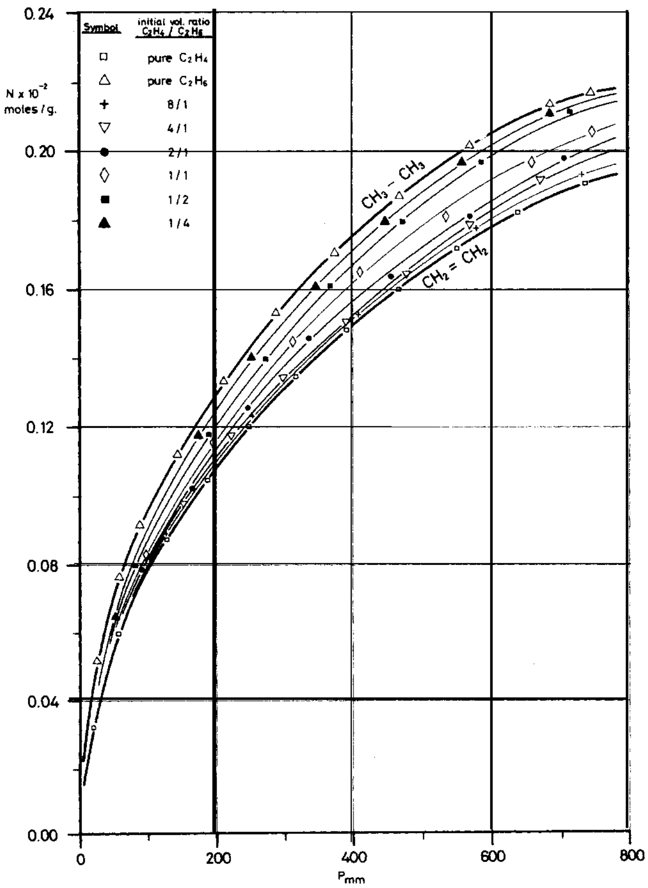


Figure 4. Equilibrium isotherms of C_2H_4 and C_2H_6 mixtures at 20°C.

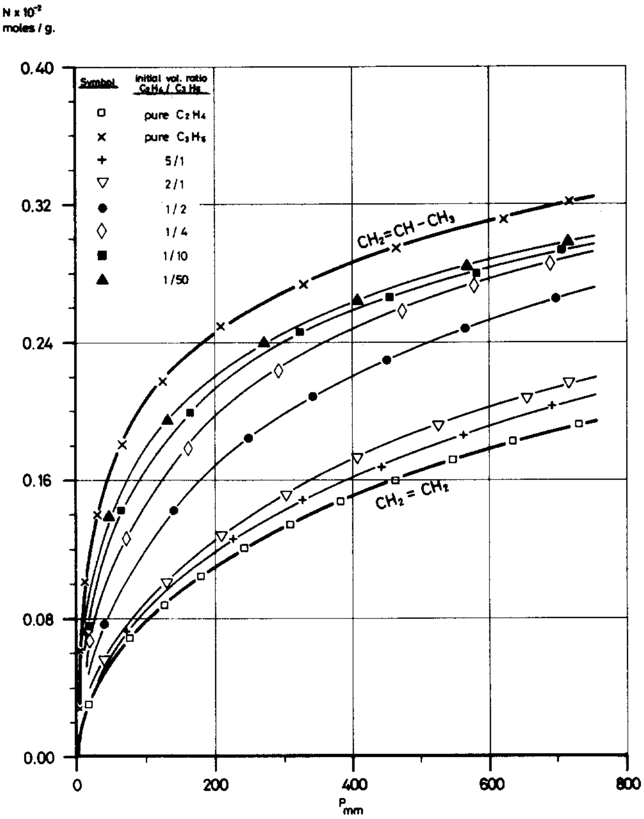


Figure 5. Equilibrium isotherms of C_2H_4 and C_3H_6 mixtures at 20°C.

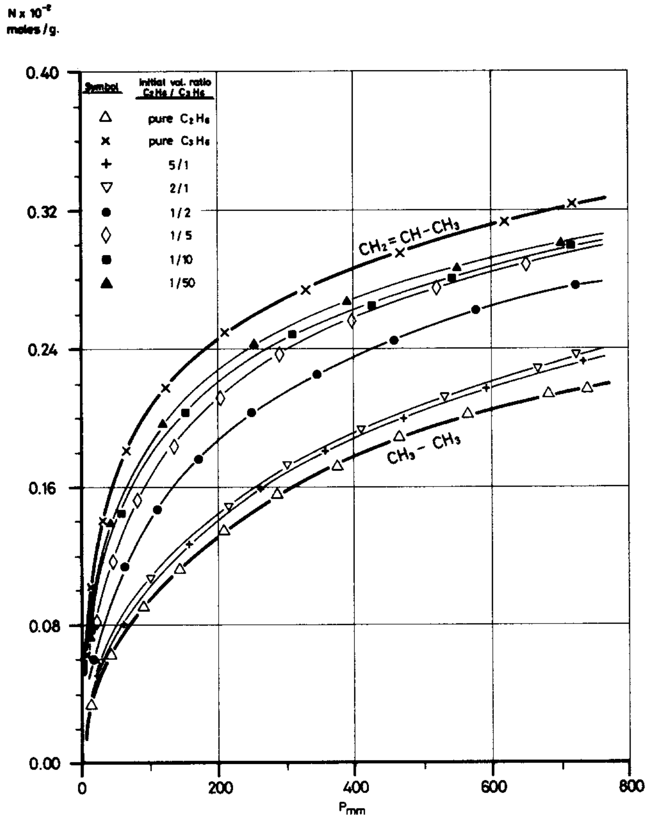


Figure 6. Equilibrium isotherms of C_2H_6 and C_3H_6 mixtures at 20°C

TABLE 2. EXPERIMENTAL EQUILIBRIUM DATA, SPREADING PRESSURE AND $p_i^0(\pi)$ OF BINARY MIXTURES

x_1	y_1	$\frac{\Pi y_1 y_2 A}{RT}$ (gmol)	$p_1^0(\Pi)$ (mm Hg)	$p_2^0(\Pi)$ (mm Hg)
		Methane-Ethylene		
0.939	0.998	$6.010\ 10^{-3}$	85.0	4.2
0.818	0.991	$7.008\ 10^{-3}$	99.0	5.0
0.632	0.974	$9.088\ 10^{-3}$	132.0	6.5
0.144	0.787	$2.900\ 10^{-2}$	520.0	20.0
0.063	0.539	$4.252\ 10^{-2}$	844.3	38.4
		Methane-Ethane		
0.848	0.998	$6.370\ 10^{-3}$	90.0	1.15
0.728	0.996	$7.373\ 10^{-3}$	105.0	1.38
0.546	0.987	$9.999\ 10^{-3}$	141.2	2.31
0.380	0.975	$1.364\ 10^{-2}$	204.0	3.15
0.116	0.790	$4.050\ 10^{-2}$	755.0	18.20
0.051	0.580	$5.450\ 10^{-2}$	1421.6	33.50
		Ethylene-Ethane		
0.880	0.931	$6.382\ 10^{-2}$	80.0	44.0
0.770	0.857	$6.640\ 10^{-2}$	85.0	48.5
0.649	0.762	$6.924\ 10^{-2}$	89.5	51.3
0.478	0.620	$7.224\ 10^{-2}$	97.5	56.7
0.314	0.444	$7.584\ 10^{-2}$	106.9	60.0
0.153	0.243	$7.967\ 10^{-2}$	118.0	67.5
		Ethylene-Propylene		
0.800	0.993	$7.200\ 10^{-2}$	97.0	4.0
0.614	0.980	$8.426\ 10^{-2}$	130.2	5.4
0.253	0.858	$1.352\ 10^{-1}$	319.5	16.5
0.141	0.696	$1.701\ 10^{-1}$	505.0	28.5
0.055	0.436	$2.072\ 10^{-1}$	847.7	46.0
0.028	0.248	$2.271\ 10^{-1}$	1024.8	58.5
		Ethane-Propylene		
0.807	0.989	$9.210\ 10^{-2}$	92.0	5.5
0.619	0.954	$1.081\ 10^{-1}$	123.0	10.5
0.277	0.798	$1.536\ 10^{-1}$	257.0	23.5
0.126	0.565	$1.922\ 10^{-1}$	424.5	38.8
0.064	0.363	$2.156\ 10^{-1}$	557.0	51.9
0.021	0.156	$2.348\ 10^{-1}$	735.0	63.9

Ternary Mixtures: methane-ethylene-ethane and ethylene-ethane-propylene.

The experimental results for the pure components are summarized in Columns 1 and 2 of Table 1. These data, substituted in Eq. 4, allowed the calculation of the spreading pressure of each pure component, which appears as $\Pi^0 A/RT$ in Column 3 of the table.

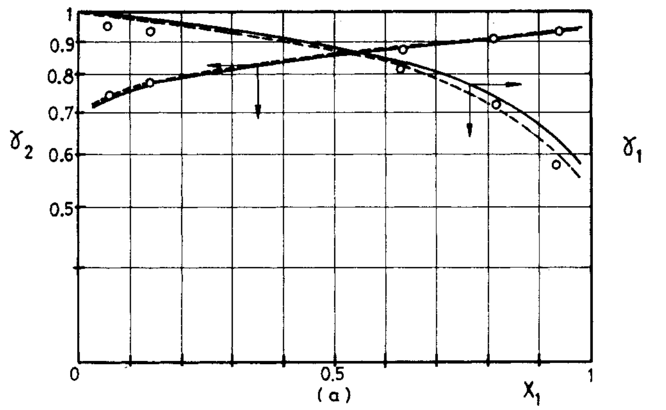
The experimental data for the binary mixtures of different initial composition are represented in figures 2 to 6. To calculate the spreading pressure of a certain mixture at a given temperature and pressure, Eqs. 5 and 6 were applied to all the points in the series of isotherms corresponding to such a pressure for the binary mixture considered. The equilibrium pressures selected were 75 and 100 mm Hg respectively. Higher pressures were not suitable for the graphical method of calculation of $p_i^0(\Pi)$ explained before, because the values of $\Pi A/RT$ were too high and considerable extrapolation of the lower curves would have been necessary.

For the five binary mixtures investigated and an equilibrium pressure of 75 mm Hg, Table 2 shows: composition of both phases (x_1, y_1), spreading pressures of the adsorbate in the form of $\Pi y_1 y_2 A/RT$, and calculated values of $p_i^0(\Pi)$ for the two components. Columns 1, 2, 4 and 5 of Table 2 were used with Eq. 7 to calculate the activity coefficients that are represented in the Figures 7a) to 11a).

Binary Mixture Equilibria: Experimental Results vs. Wilson and UNIQUAC Equations

The constants Λ_{ij}, Λ_{ji} and τ_{ij}, τ_{ji} of Eqs. 8 and 9 depend on composition and activity coefficients, and the two last ones also on the structural parameters s_i and r_i and the coordination index z.

The lack of data in the high dilution zones made unreliable to make the possible determination of such constants with the simplified equations for infinite dilution. Therefore, a nonlinear regression program applied to all the experiments of each mixture was used to calculate them.



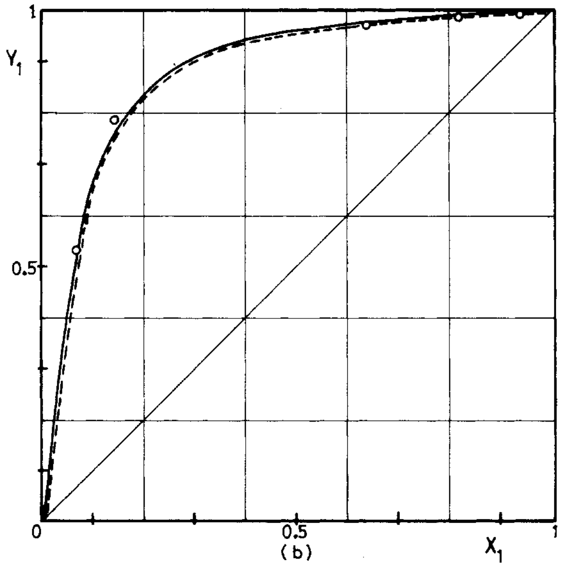


Figure 7. Mixture CH_4-C_2H_4: experimental and calculated equilibrium data.
a) Activity coefficients.
(o exp., —— WILSON, --- UNIQUAC)
b) y-x diagram (molar fractions).
(o exp., —— WILSON, --- UNIQUAC)

With the calculated values of these constants, Wilson and UNIQUAC equations were applied to the adsorbate compositions indicated in Table 2, for calculating the activity coefficients. The resulting values are also represented in Figures 7a) to 11a). Finally, with the calculated activity coefficients and Eq. 7, gas phase compositions corresponding to Column 1 of Table 2 were obtained. The calculated and experimental results for 20°C and 75 mm Hg are compared in Figures 7b) to 11b). The deviations between experimental and calculated data were always less than 5%.

Activity coefficients of Figures 7a)-11a) show a clear deviation from ideality in all the cases except for the binary mixture of ethane-ethylene. This is obviously due to the differences between the molecules of the components, showing different adsorption capacities, and competition to occupy the active centers of the adsorbent surface. In the case of the ethylene-ethane mixture (Figure 9), the activity coefficients of both components were practically equal to unity due to their similar adsorption capacities.

Finally, we want to point out that the values of r, s, and z parameters used in UNIQUAC equation were the same as the ones proposed by Abrams and Prausnitz (1975) for the components in the liquid phase with the same composition. The small deviations observed between experimental and calculated values demonstrate the viability of such a hypothesis.

Prediction of Ternary Mixtures Equilibria: Wilson and UNIQUAC Equations

Two ternary mixtures were studied: methane-ethylene-ethane and ethylene-ethane-propylene, for which experimental and predicted equilibrium data were obtained.

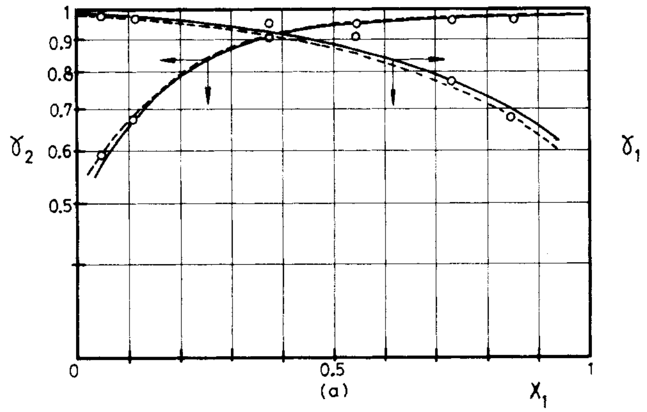
For predicting the composition of the gaseous phase corresponding to a given composition of the adsorbed phase, Wilson and UNIQUAC equations were used again. These equations, with the constants previously calculated for binary mixtures (Λ_{ij}, Λ_{ji}, τ_{ij}, τ_{ji}), provided the necessary activity coefficients of the three adsorbed components. Then, the spreading pressure of the mixture was estimated by a trial-and-error method, trying values of p_i^0 (Π) and the activity coefficients just calculated in the modified Raoult's Eq. 7, until the necessary condition $y_1 + y_2 + y_3 = 1$ was satisfied.

Table 3 summarizes the experimental and calculated molar fractions of both phases at equilibrium. The agreement attained with both equations was similar to that for binary mixtures.

Although a broader range of compositions was intended with both ternary mixtures, very dilute mixtures of the less adsorbible components (methane in one of the mixtures and ethane in the other) resulted in large spreading pressures which made the graphic calculation of p_i^0 (Π) unsuitable, as already mentioned.

The composition ranges investigated with both ternary mixtures are considered to be sufficiently representative to let us conclude that the precision attained in the prediction of equilibrium data with both equations, Wilson and UNIQUAC, is valid for any reasonable composition of the two mixtures.

For the pure components, the five binary mixtures and the two ternary mixtures, the corresponding isotherms at 50°C were



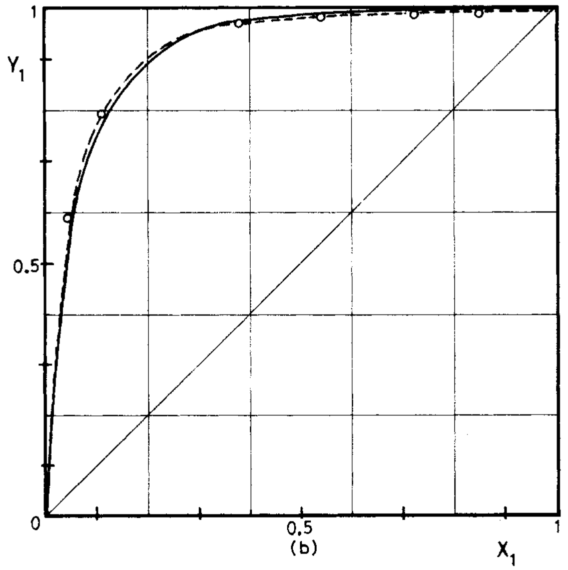


Figure 8. Mixture CH_4-C_2H_6: experimental and calculated equilibrium data.
a) Activity coefficients.
(o exp., —— WILSON, ---- UNIQUAC)
b) y-x diagram (molar fractions).
(o exp., —— WILSON, ---- UNIQUAC)

TABLE 3. EXPERIMENTAL AND CALCULATED EQUILIBRIUM DATA FOR TERNARY MIXTURES

		Experimental					Wilson			UNIQUAC	
x_1	x_2	x_3	y_1	y_2	y_3	y^w_1	y^w_2	y^w_3	y^u_1	y^u_2	y^u_3
					Methane-Ethylene-Ethane						
0.376	0.309	0.315	0.950	0.035	0.015	0.946	0.038	0.017	0.943	0.041	0.016
0.276	0.239	0.484	0.921	0.033	0.046	0.920	0.043	0.038	0.909	0.045	0.046
0.275	0.480	0.244	0.899	0.085	0.016	0.897	0.084	0.018	0.885	0.096	0.019
0.161	0.417	0.422	0.790	0.113	0.080	0.814	0.117	0.068	0.769	0.152	0.079
0.113	0.582	0.305	0.685	0.250	0.065	0.694	0.243	0.065	0.661	0.271	0.068
0.113	0.293	0.594	0.710	0.138	0.152	0.732	0.132	0.136	0.687	0.148	0.166
0.091	0.445	0.464	0.633	0.230	0.137	0.653	0.222	0.124	0.593	0.258	0.149
					Ethylene-Ethane-Propylene						
0.800	0.180	0.020	0.889	0.110	0.001	0.887	0.112	0.001	0.889	0.110	0.001
0.629	0.174	0.197	0.865	0.124	0.011	0.854	0.137	0.009	0.850	0.139	0.010
0.559	0.205	0.236	0.810	0.175	0.014	0.806	0.182	0.012	0.812	0.176	0.012
0.455	0.251	0.294	0.734	0.245	0.021	0.735	0.247	0.018	0.740	0.244	0.016
0.397	0.437	0.166	0.604	0.387	0.009	0.602	0.391	0.008	0.602	0.387	0.011
0.291	0.324	0.385	0.573	0.388	0.039	0.567	0.399	0.034	0.571	0.398	0.031
0.226	0.483	0.291	0.394	0.583	0.022	0.428	0.554	0.019	0.431	0.553	0.017
0.187	0.582	0.231	0.332	0.656	0.012	0.341	0.646	0.013	0.344	0.642	0.013

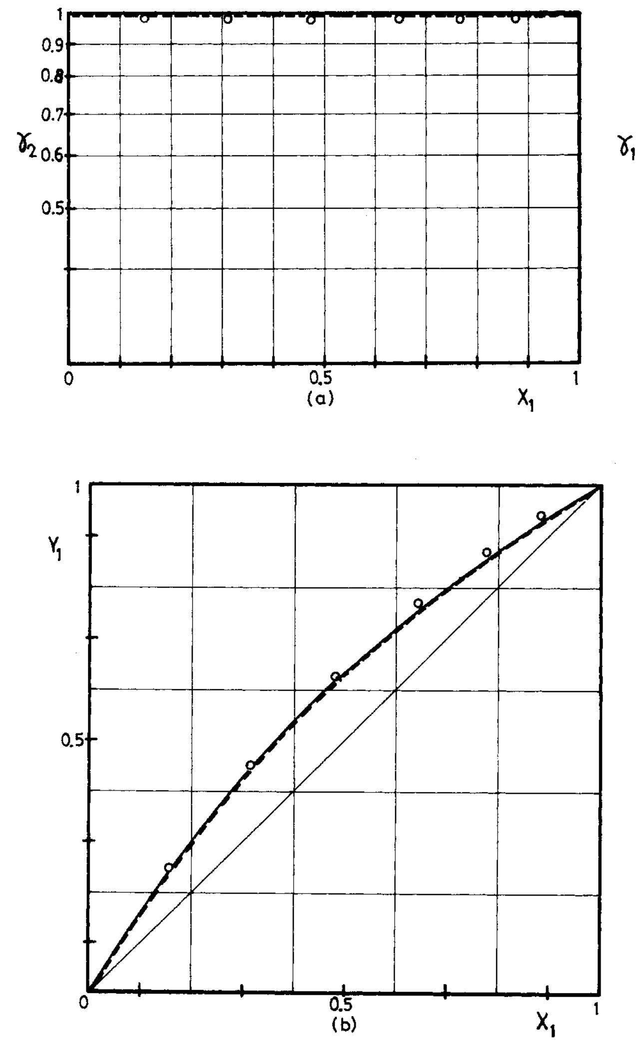


Figure 9. Mixture C_2H_4-C_2H_6: experimental and calculated equilibrium data.
a) Activity coefficients.
(o exp., —— WILSON, --- UNIQUAC)
b) y-x diagram (molar fraction).
(o exp., —— WILSON, --- UNIQUAC)

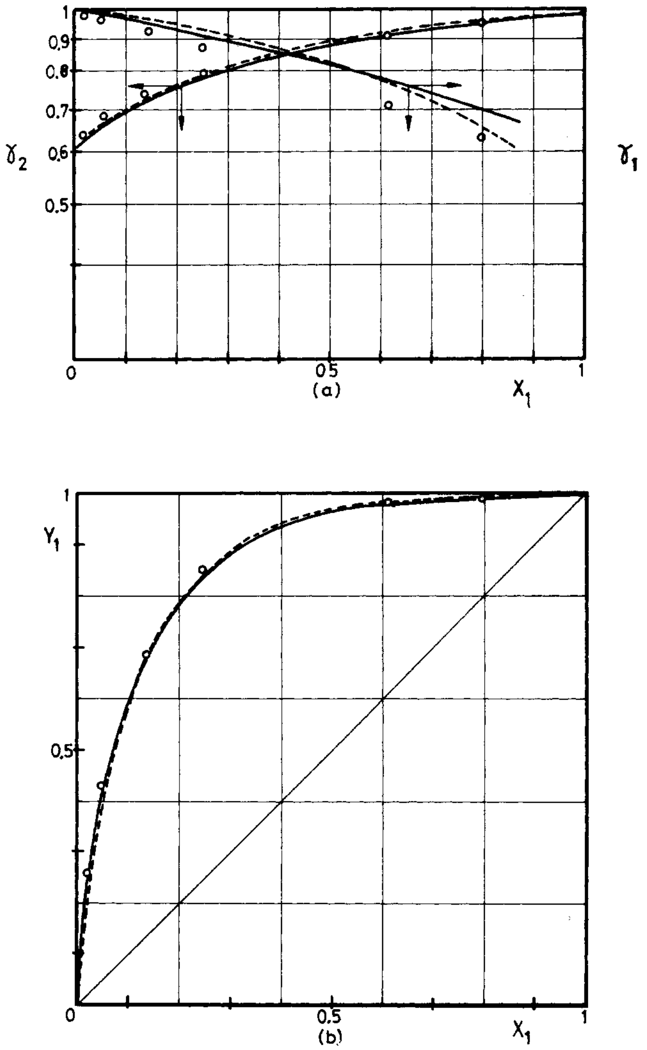


Figure 10. Mixture C_2H_4-C_3H_6:. experimental and calculated equilibrium data.
a) Activity coefficients.
(o exp., —— WILSON, --- UNIQUAC)
b) y-x diagram (molar fractions).
(o exp., —— WILSON, --- UNIQUAC)

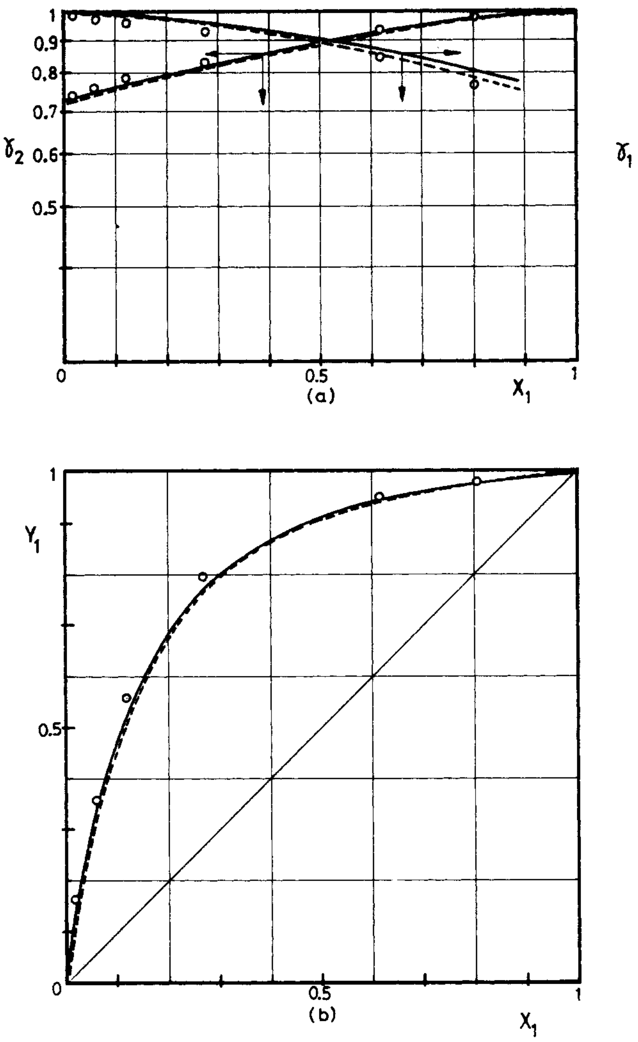


Figure 11. Mixture C_2H_6-C_3H_6: experimental and calculated equilibrium data.
a) Activity coefficients.
(o exp., —— WILSON, --- UNIQUAC)
b) y-x diagram (molar fractions).
(o exp., —— WILSON, --- UNIQUAC)

also experimentally determined. At both temperatures (20 and 50°C), the equilibrium data of the binary and ternary mixtures were calculated for 75 and 100 mm Hg. Deviations between experimental and calculated values were in all cases of the same order of magnitude already indicated (Marrón, 1979).

NOTATION

A = total area of adsorbent
c = component c
G = Gibbs free energy
H = enthalpy
l = function of parameters z, r, s in UNIQUAC equation
N = number of moles adsorbed per gram of adsorbent
N_i = number of moles adsorbed of component i
N_t = number of total moles adsorbed
p = pressure
$p_i^0(\Pi)$ = equilibrium pressure for pure component, i, corresponding to spreading pressure Π
R = gas constant
r = structural parameter in UNIQUAC equation
s = structural parameter in UNIQUAC equation
T = absolute temperature
V = total volume
x = molar fraction in adsorbed phase
y = molar fraction in gas phase
z = coordination index of individual molecules in UNIQUAC equation

Geek Letters

Δ = increment
ϕ = function of parameters r, x in UNIQUAC equation
γ = activity coefficient
Λ = binary constant in Wilson equation
μ_i = chemical potential of component i
Π = spreading pressure of the mixture
Π_i = spreading pressure of pure component i
τ = binary constants in UNIQUAC equation
θ = function of paramenters s, x, in UNIQUAC equation

Superscripts

a = adsorbed phase
g = gas phase
0 = pure component

Subscripts

i = component i
j = component j
k = component k

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