

Adsorption of Gas Mixtures on Solid Surfaces, Theory and Computer Simulation

ROGER F. CRACKNELL AND DAVID NICHOLSON

Department of Chemistry, Imperial College of Science, Technology and Medicine, London SW72AY, United Kingdom

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Abstract. A treatment of the thermodynamics of mixed gas adsorption is presented in which the gas-solid interface is three dimensional. Such a treatment yields an additional term as compared to two dimensional approaches. This additional term has significant consequences for the derivation of adsorbed solution theories, particularly at higher temperatures.

Results are presented for a Grand Canonical Monte Carlo study of a model methane-ethane mixture in a carbonaceous slit pore. Comparison of single component and mixture results provides an unambiguous means of testing theories of adsorbed solutions and bears out the thermodynamic treatment presented in the previous section of the paper.

Introduction

In the chemical industry, separation of a mixture of gases is most frequently carried out by liquefaction of the mixture, followed by distillation. An alternative approach is to separate gases by selective adsorption of one species. Keller (1983) has listed the criteria which make an adsorptive separation preferable to a cryogenic one; the most important criterion is the effectiveness of the separation. For a cryogenic process this can be quantified by the relative volatility (which for an ideal binary mixture is the ratio of the vapour pressures of the two mixture components), whilst for an adsorptive separation, the analogous quantity is the separation factor, S (sometimes called α) which is given by

$$S = \frac{x_i/x_j}{y_i/y_j} \quad (1)$$

where x_i and y_i are the adsorbed phase and bulk gas phase mole fraction respectively of component i , and x_j and y_j , are the adsorbed phase and bulk gas mole fractions of component j respectively. Because of the high cost of compressors, separation factors tend to have to be reasonably high to make an adsorption process viable as compared to cryogenic methods.

Nevertheless, both air drying and N_2/O_2 separation are carried out commercially by pressure swing adsorption methods.

The viability of any adsorption process depends primarily, therefore on the separation factor. The well

known ideal adsorbed solution theory (IAST) of Myers and Prausnitz (1965) enables separation factors to be predicted from single component isotherms, recent modifications to the method (Costa et al., 1981, Valenzuela et al., 1988) allow for non-ideality of the adsorbed phase. Many treatments of the thermodynamics of mixture adsorption (e.g. Myers and Prausnitz, 1965; Van Ness, 1969; Sievers and Mersmann, 1993) have viewed the adsorbed phase as two dimensional and the adsorbed solution theory is developed on this basis. In this work we have treated the gas-solid interface as a three dimensional system (Young and Crowell, 1962; Steele, 1972; Nicholson and Parsonage, 1982) and have developed the thermodynamics of adsorbed solutions from this viewpoint. We have also examined the thermodynamic consequences of using excess adsorption isotherms (rather than the total amount in the adsorbed phase) on the IAST.

Over the last 15 years or so, with the advent of fast computers, it has been possible to solve the statistical mechanics of adsorption problems exactly by use of Monte Carlo and Molecular Dynamics techniques (Nicholson and Parsonage, 1982) and recently these have been extended to mixture adsorption (Finn and Monson, 1992; Karavias and Myers, 1991; Maddox and Rowlinson, 1993; Razmus and Hall, 1991; Cracknell et al., 1993; 1994). Various density functional theories for mixture adsorption have also been developed (Tan and Gubbins, 1992; Kierlik and Rosinberg, 1992) which are more numerically tractable than

full simulations and have been used to give important new insights into the way selectivity varies with pressure for a number of model systems.

Simulation methods can also play an important role in the development and testing of theories. It is possible to directly simulate both mixture as well as single component adsorption. By comparing the results of mixture and single component simulations it is possible to check that the simulations are consistent with theories based on the thermodynamics of mixture adsorption. In this work we present a grand canonical Monte Carlo simulation of a methane-ethane mixture in a carbonaceous slit pore, and compare the results from the simulation with our thermodynamic treatment.

Theory

Thermodynamics of Mixture Adsorption on Plane Surfaces

Consider the thermodynamic system shown in Fig. 1, it extends from the Gibbs' dividing surface at the gas-solid interface into a region of uniform gas; it contains N_i moles of component i . The fundamental thermodynamic equation for the change in internal energy, dU , of this system is

$$dU = TdS + dW + \sum_i \mu_i dN_i \quad (2)$$

where T is the temperature, dS the entropy change and μ_i is the chemical potential of component i . The term dW is the work done by the system on its surroundings,

$$dW = -pdV - \pi dA \quad (3)$$

where the first term on the RHS of (3) is the work done by the system when it expands by an amount dV (equivalent to $A dl$) in a direction normal to the surface against a bulk external pressure, p , whilst maintaining the area, A , of the gas-solid interface. The second term on the RHS of (3) is the work done, against the external spreading pressure π , in increasing the interfacial area by an amount dA . Taking (2) and (3) together and integrating over the extensive variables one obtains

$$U = TS - PV - \pi A + \sum_i \mu_i N_i \quad (4)$$

Following Nicholson and Parsonage (1982), the discussion will proceed by considering the grand free energy,

Ω , defined by the equation

$$\Omega = U - TS - \sum_i \mu_i N_i \quad (5)$$

Taking the differential form of (5) and combining it with (2) yields

$$d\Omega = -SdT - pdV - \pi dA - \sum_i N_i d\mu_i \quad (6)$$

Alternatively, by combining (4) and (5), we can write for the grand free energy

$$\Omega = -\pi A - pV \quad (7)$$

which on differentiation yields

$$d\Omega = -pdV - Vdp - \pi dA - Ad\pi \quad (8)$$

Subtracting (8) from (6) gives:

$$\sum_i N_i d\mu_i = -SdT + Ad\pi + Vdp. \quad (9)$$

An identical expression can also be derived easily using the Gibbs' function (Young and Crowell, 1962; Steele, 1972 [p. 82]). We note that if the adsorbed phase is considered as a purely two dimensional system (Myers and Prausnitz, 1965; Van Ness, 1969) then the " Vdp " term is absent. At sufficiently low temperatures, the density in the bulk gas (in equilibrium with the adsorbed system) is negligible compared to adsorbate density and the term can be safely ignored (Rudishill and LeVan, 1992). In order to keep our thermodynamics general, we retain this term and later show that it is quite important.

Equation (9) has several important thermodynamic consequences; if we consider adsorption of a single component and make the substitution

$$d\mu = RT d \ln p \quad (10)$$

then at constant temperature

$$Ad\pi = NRT d \ln p - Vdp \quad (11)$$

We can write the total number of moles in the system, N , as the number of moles which would be present in the system in the absence of the surface, N^{NA} (where superscript " NA " stands for "non-adsorbing"), plus the surface excess number of moles, N^Σ , thus

$$N = N^{NA} + N^\Sigma \quad (12)$$

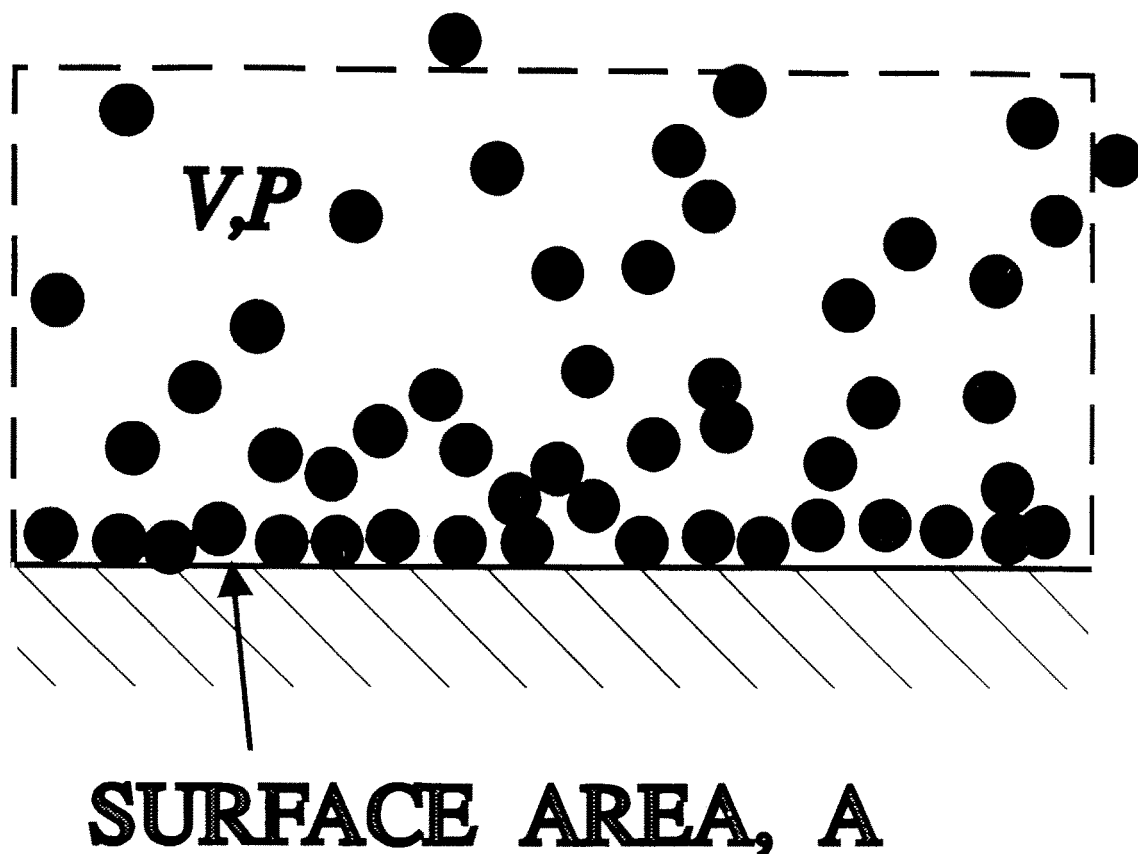


Fig. 1. Thermodynamic system for a gas adsorbing on to a plane surface.

If it can be assumed that the gas in the system would be ideal in the absence of the interface we can write

$$V = \frac{N^N A RT}{p} \quad (13)$$

Equations (12) and (13) can then be substituted into (11) to yield

$$Ad\pi = N^\Sigma RT d \ln p \quad (14)$$

which is the familiar Gibbs' adsorption isotherm. However this treatment illustrates that the Gibbs' adsorption isotherm refers to *excess* number of moles (Nicholson and Parsonage, 1982, p. 30).

To illustrate a further thermodynamic consequence of (9), we introduce a new thermodynamic parameter, Φ , which is defined as

$$\Phi = \frac{V}{A} p + \pi \quad (15)$$

where V is the volume of the thermodynamic system and A the area of the gas-solid interface. We note that

in some texts the spreading pressure (which we call π) is denoted as ϕ , this is pointed out to avoid possible confusion. Now clearly, if the volume and area are constant

$$Ad\Phi = Vdp + Ad\pi \quad (16)$$

and (9) can be rewritten as

$$\sum_i N_i d\mu_i = -SdT + Ad\Phi \quad (17)$$

At constant Φ and T , this is the analogue of the Gibbs Duhem equation for an adsorbed phase

$$\sum_i N_i d\mu_i = 0 \quad (18)$$

Therefore we require constancy of Φ and T , and not π and T in order to be able to treat the thermodynamic system as an ideal solution.

One can then follow the standard derivation of the ideal adsorbed solution theory (Myers and Prausnitz, 1965), using Φ and not the spreading pressure π , thus

for the chemical potential of component i in the adsorbed phase, one writes

$$\mu_i(T, \Phi, x_i, \dots) = \mu_i^0(T) + RT \ln[p_i^0(\Phi)] + RT \ln x_i \quad (19)$$

where $\mu_i^0(T)$ is the standard chemical potential of i at temperature T (i.e. in the perfect gas state at a pressure of 1 atm), $p_i^0(\Phi)$ is the bulk pressure of component i which would give rise to that particular value of Φ when i is the only component and x_i is the adsorbed phase mole fraction of i , or more accurately the mole fraction of i in the adsorbed phase. Similarly, one can write for the bulk gas phase of i

$$\mu_i(T, \Phi, y_i) = \mu_i^0(T) + RT \ln p y_i \quad (20)$$

where y_i is the gas phase mole fraction. Combining (19) and (20) yields the condition

$$p y_i = p_i^0(\Phi) x_i \quad (21)$$

which is the basic IAS equation but written in terms of Φ .

For single component adsorption (9) with (17) at constant T leads to

$$A d\Phi = N R T d \ln p \quad (22)$$

which is analogous to the Gibbs' adsorption isotherm, but N refers to the total number of moles in the system, not the excess. One can calculate Φ from the integral

$$\frac{A\Phi}{RT} = \int_0^p N d \ln p \quad (23)$$

Comparison of Φ and π

In the previous section we have proposed that for an adsorbed phase to be treated as an ideal solution, the calculations should be made not at constant spreading pressure π , but rather at a constant value of a new thermodynamic variable, Φ as determined in (17). The spreading pressure, π , can be written in terms of the diagonal components of the pressure tensor (Steele, 1972, p. 104), thus

$$\pi A = \int_V \left\{ \frac{1}{2} [p_{xx}(\mathbf{r}) + p_{yy}(\mathbf{r})] - p_{zz}(\mathbf{r}) \right\} d\mathbf{r} \quad (24)$$

where the integral is over the whole thermodynamic system in Fig. 1, i.e. from the Gibbs' surface at the gas-solid interface to a domain of uniform density. For adsorption on a single surface, mechanical stability requires that the component of the pressure tensor normal

to the surface, p_{zz} be equal to the bulk pressure, thus it can be easily seen that for the case of adsorption on a plane surface,

$$\Phi A = \int_V \frac{1}{2} [p_{xx}(\mathbf{r}) + p_{yy}(\mathbf{r})] d\mathbf{r} \quad (25)$$

and Φ is simply related to the transverse components of the pressure tensor.

Thermodynamics of Mixture Adsorption in Slit Shaped Pores

In the discussion so far, we have been referring to adsorption on a plane surface. The discussion can easily be extended to considering fluids in slit shaped pores. (See Fig. 2) The thermodynamic system now consists of a pore and is bounded by Gibbs' dividing surfaces at the gas-solid interface on the opposite walls of the pore, these dividing surfaces being separated by a pore dimension, H' . Thus the volume, V_{pore} of the system is equal to AH' . Equation (2) remains valid, however dW is now written as

$$dW = -p_{zz} dV_{\text{pore}} - \pi dA \quad (26)$$

where it is recognised that in a pore, the normal component of the pressure tensor, p_{zz} , is not necessarily equal to the bulk pressure. In this form, the spreading pressure is given by

$$\pi = \int_0^{H'} \left\{ \frac{1}{2} [p_{xx}(z) + p_{yy}(z)] - p_{zz}(z) \right\} dz \quad (27)$$

Substituting (26) into (2) and taking the differential form of (4), we obtain

$$d\Omega = -SdT - p_{zz} dV_{\text{pore}} - \pi dA - \sum_i N_i d\mu_i \quad (28)$$

We can write for the grand potential

$$\Omega = -\pi A - p_{zz} V_{\text{pore}} \quad (29)$$

which on differentiation yields

$$d\Omega = -p_{zz} dV_{\text{pore}} - V_{\text{pore}} dp_{zz} - \pi dA - A d\pi \quad (30)$$

Subtracting (30) from (28) gives:

$$\sum_i N_i d\mu_i = -SdT + A d\pi + V_{\text{pore}} dp_{zz} \quad (31)$$

The new thermodynamic parameter, Φ , is now

$$\Phi = H' p_{zz} + \pi \quad (32)$$

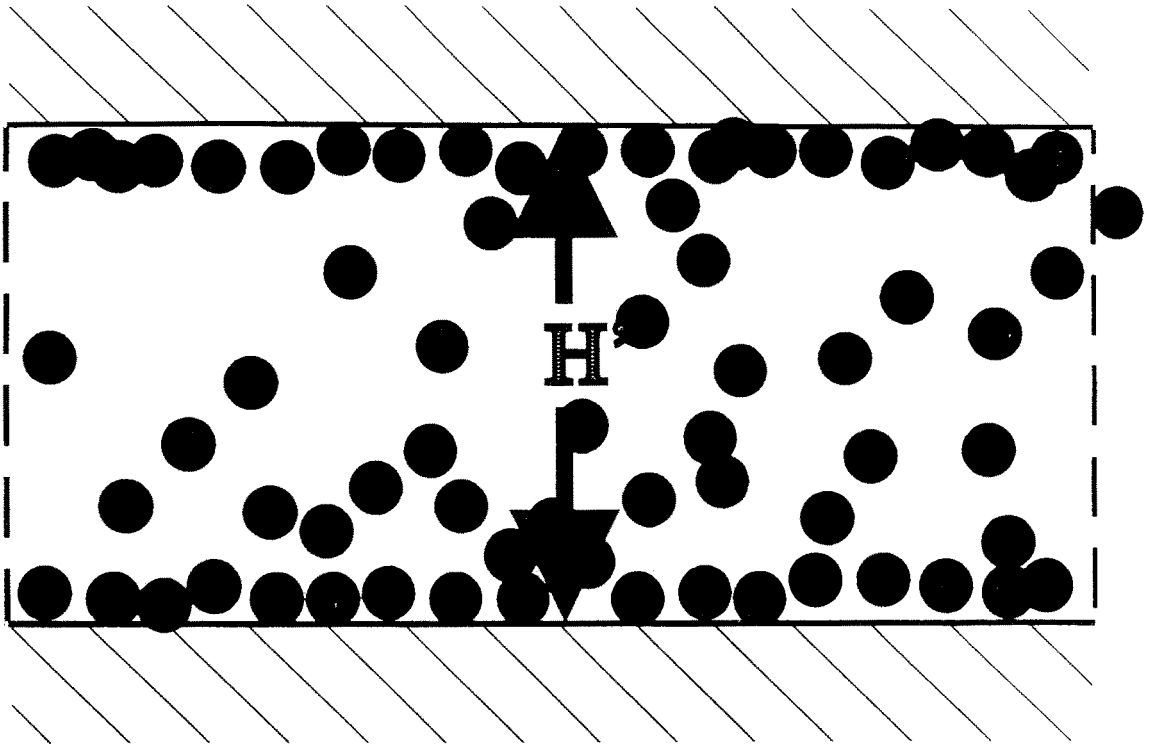


Fig. 2. Thermodynamic system for gas adsorption in a micropore.

then at constant pore width

$$Ad\Phi = Ad\pi + V_{\text{pore}}dp_{zz} \quad (33)$$

and therefore

$$\sum_i N_i d\mu_i = -SdT + Ad\Phi \quad (34)$$

and the argument for developing an ideal adsorbed solution theory at constant Φ can proceed as before (Eqs. 19 through 23), where Φ for a single component isotherm may be calculated using (23).

Obtaining the spreading pressure, π , is more problematic for a pore (although as we have demonstrated, it is Φ not π which is needed for the ideal adsorbed solution theory). The procedure leading to the derivation of the Gibbs' adsorption isotherm for a plane surface (Eqs. 12 to 14) can only be extended to pores if it can be assumed that the normal pressure, p_{zz} in the pore is equal to the bulk pressure, p . While this is valid for pores of a sufficient size, it is certainly not true for micropores as evidenced by the oscillatory solvation forces seen by computer simulations (e.g. Balbuena et al., 1993) and experiments using the surface force apparatus (Israelachvili, 1992).

Simulation

Method

From the theory developed in the previous section, the ideal adsorbed solution theory requires that the adsorbed mixture be at a constant value of the thermodynamic parameter, Φ , rather than spreading pressure, π . The former is determined using the *analogue* of Gibbs adsorption isotherm given in Eq. 23 based on the total number of molecules in the system rather than the excess amount adsorbed, which appears in the Gibbs' adsorption isotherm (Eq. 14).

Using the techniques of molecular simulation, one can determine exactly an adsorption isotherm which corresponds to a particular model for the intermolecular interactions in the system (i.e. both the gas-solid and gas-gas interactions). The grand ensemble is the most convenient Gibbsian ensemble for adsorption problems because the chemical potential of the components in the system (as well as the volume and temperature) are specified in advance, and the equilibrium number of particles of any particular species present in the system is calculated as an ensemble average. The Grand

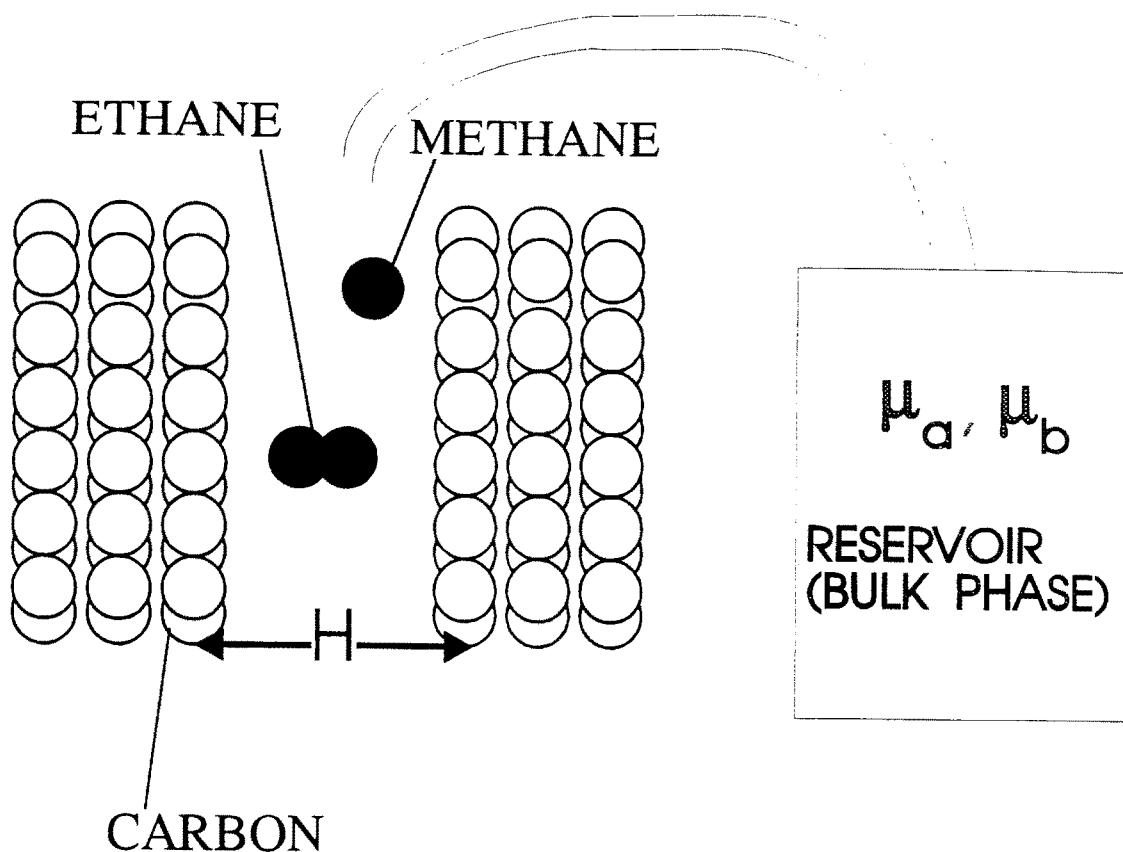


Fig. 3. Models used in simulation.

Canonical Monte Carlo (GCMC) technique establishes an algorithm which generates a Markov chain of grand ensemble configurations; equilibrium properties can be calculated as averages over a number of configurations in the simulation.

Our basic approach is to use GCMC to calculate single component isotherms for methane and ethane adsorption in a model carbonaceous slit micropore. The IAS is then used to predict mixture properties, which can be compared with simulated results for a mixture. One can thereby obtain a completely self-consistent and unambiguous test of the IAS.

Full details of the GCMC technique for mixtures are described elsewhere (Cracknell et al., 1993); the three usual GCMC trials (Nicholson and Parsonage, 1982; Allen and Tildesley, 1987) were included in the simulation, namely attempts to move particles in the system, attempts to create particles, and attempts to delete particles from the system. To these were added a fourth type of trial, namely attempts to swap the identities of particles in the simulation. It was

found that although this fourth type of trial was not strictly necessary for convergence of the Markov chain, it led to a large improvement in the statistical accuracy of ensemble averages for a given number of configurations.

The model used for our simulation is shown in Fig. 3. Methane was modelled as a spherical Lennard-Jones site, ethane as two Lennard-Jones sites separated by a fixed bond length, l . The Lennard-Jones (12-6) potential is given by

$$u_{ij} = -4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} \right] \quad (35)$$

The interactions were cut (but not shifted) at 1.756 nm (5 times the ethane σ parameter). The parameters used in the simulation are given in Table I.

The graphitic surface was treated as stacked planes of Lennard-Jones atoms. The interaction energy between a fluid particle and a single graphite surface is given by

Table I. Potential parameters used in the simulations.

Pair	σ/nm	ϵ/k_B	l/nm	ref
CH ₄ -CH ₄	0.381	148.1 K	–	Steele, 1972
C ₂ H ₆ -C ₂ H ₆ (2CLJ)	0.3512	139.81 K	0.2353	Fischer et al., 1989
C(graphite)- C(graphite)	0.340	28.0 K	–	Steele, 1972

the 10-4-3 potential of Steele (1972)

$$u_{\text{sf}}(z) = 2\pi\rho_s\epsilon_{\text{sf}}\sigma_{\text{sf}}^2\Delta \left\{ \frac{2}{5} \left(\frac{\sigma_{\text{sf}}}{z} \right)^{10} - \left(\frac{\sigma_{\text{sf}}}{z} \right)^4 - \frac{\sigma_{\text{sf}}^4}{3\Delta(0.61\Delta + z)^3} \right\} \quad (36)$$

where Δ is the separation between graphite layers ($= 0.335$ nm) and ρ_s is the number of carbon atoms per unit volume in graphite (114 nm⁻³). σ_{sf} and ϵ_{sf} are the solid-fluid Lennard-Jones parameters which were calculated by combining the graphite parameters in Table I with the appropriate fluid parameters using the Lorentz-Berthelot rules. The external field, $u^{(1)}$, in a slit pore of width H is the sum of the interactions with both graphitic surfaces and can be expressed mathematically as

$$u^{(1)} = u_{\text{sf}}(z) + u_{\text{sf}}(H - z) \quad (37)$$

H is the distance between the carbon centres on adjacent graphitic planes, note that H is larger than H' (see below).

We have shown elsewhere (Cracknell et al., 1994) that these models can be used to give good agreement with experimental isosteric heats for adsorption on a single surface and we have made a detailed study of the variation of separation factor with pore size, pressure and temperature for this system. For this present work, we are using simulation merely as a test of the veracity of the conclusions based on the thermodynamics of the previous section.

The simulations were run on two Intel i860 processors connected to a 486 PC front end. A typical simulation with 200 particles took approximately 2 hours for 5×10^6 configurations, although the number of particles in the simulation varied with the particular point on the adsorption isotherm being simulated.

Results and Discussions

Figure 4 shows simulated single component isotherms for methane and ethane at 296.2 K in a pore of width

$H = 2.5 \sigma_{\text{CH}_4}$ (0.9525 nm). For the purposes of calculating the adsorbate density in the pore (which is the units for the uptake), the volume comprised all the space between the planes of carbon centres, even though some of this is dead volume, inaccessible to the adsorbate. The full line refers to the total number of particles in the system divided by the volume, the dashed lines refer to excess numbers of particles in the system divided by the system volume. We estimated the number of particles of a nonadsorbing ideal gas that would be present in the system by assuming that the effective pore width is given by

$$H'(\text{nm}) = H(\text{nm}) - 0.24 \quad (38)$$

Although it is impossible to calculate excess quantities in a completely unambiguous way, we have shown elsewhere from looking at gas-solid potential energies in micropores that the physical size of the carbon atoms causes a reduction in the effective pore width of approximately 0.24 nm (Kaneko et al., 1994).

In Fig. 5, the solid circles are the separation factors calculated from the mixture simulation for an equimolar bulk mixture for various different pressures at 296.2 K. It is equal to the total amount of ethane in the pore divided by the total amount of methane, (note that these are not excess quantities). The solid line is the IAS prediction (Eq. 21) of the separation factor using the simulated single component total isotherms (i.e. using the parameter Φ). The IAS calculation was carried out by fitting the single component isotherms to a Langmuir Uniform Distribution (Myers, 1984). It is in very good agreement with the directly calculated mixture results. Good agreement was not observed for the IAS calculation using the excess single component isotherms (dotted line). This result appears to confirm our thermodynamic description of mixed gas adsorption, and it is clearly the thermodynamic parameter, Φ , which should be the basis of adsorbed solution theories.

It is not altogether surprising that using excess isotherms, one can not accurately predict the separa-

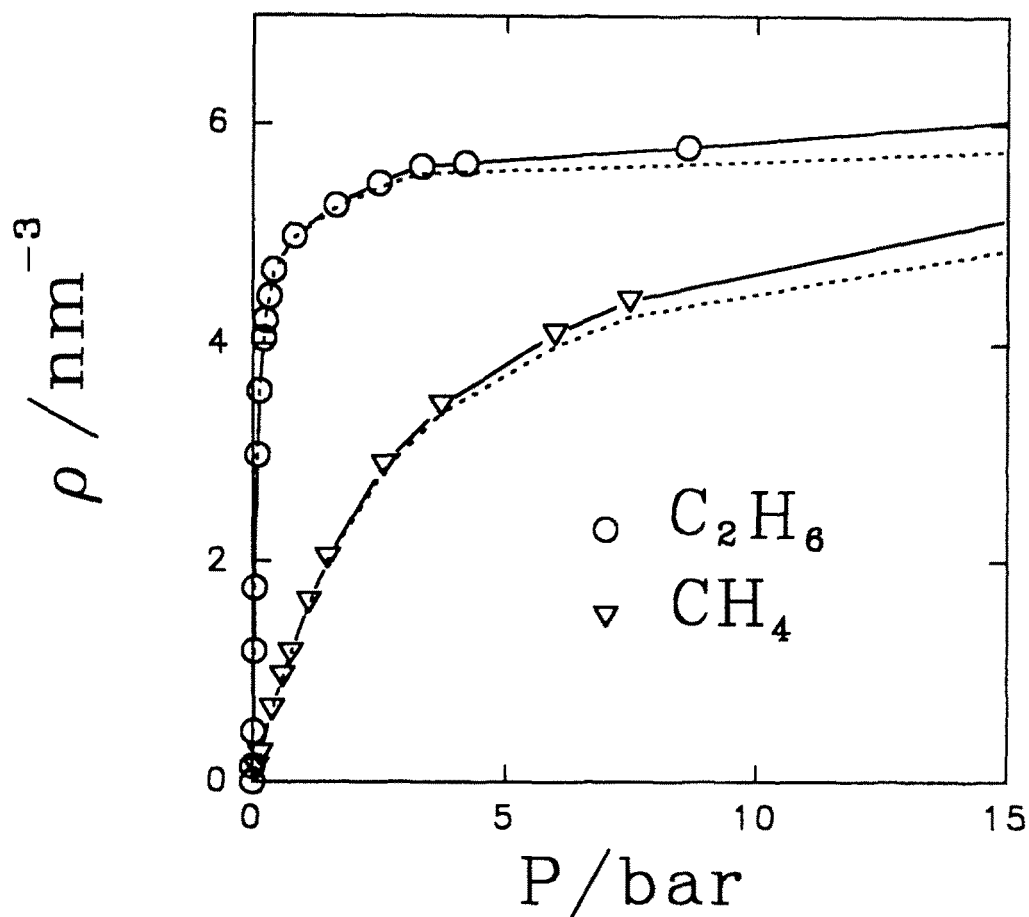


Fig. 4. Simulated single component isotherms for methane and ethane in a carbon slit pore of width $H = 2.5\sigma_{\text{CH}_4}$, $T = 296.2$ K.

tion factor (which is given by ratios of the *total* amounts of each species in the system). It is important to point out also that using excess isotherms for the IAS, one does not obtain an “excess separation factor” based on the ratio of excess amounts of each species either, instead one produces data with little or no thermodynamic meaning or significance.

Conclusions

Our thermodynamic description of mixture adsorption, using a three dimensional thermodynamic system, suggests that an ideal adsorbed solution will not have a constant spreading pressure, but rather that it is a related thermodynamic parameter, Φ , which must be constant. In practice, this means that it is the total adsorption isotherm and not the excess that is required for IAS calculations.

The Ideal Adsorbed Solution theory can provide a very accurate description of the thermodynamics of methane/ethane adsorption in carbonaceous slit pores as long as the total amount adsorbed is used and not the excess. Unfortunately in experiments (as opposed to simulation), it is the adsorption excess which is obtained by both the gravimetric and volumetric methods, therefore it is necessary to obtain total isotherms by adding on a correction term. The pore volume is obviously required for such a correction, something which can be obtained by helium replacement methods or by the α_s method [Gregg and Sing, 1982].

It should be mentioned that the spectacular discrepancy between the two predictions of S in Fig. 5 is likely to be reduced or even to disappear at low temperature, when the number of gas phase molecules in the pore space would be much smaller than the number adsorbed. We have not investigated this point in detail. It is, however, tempting to speculate whether in cases

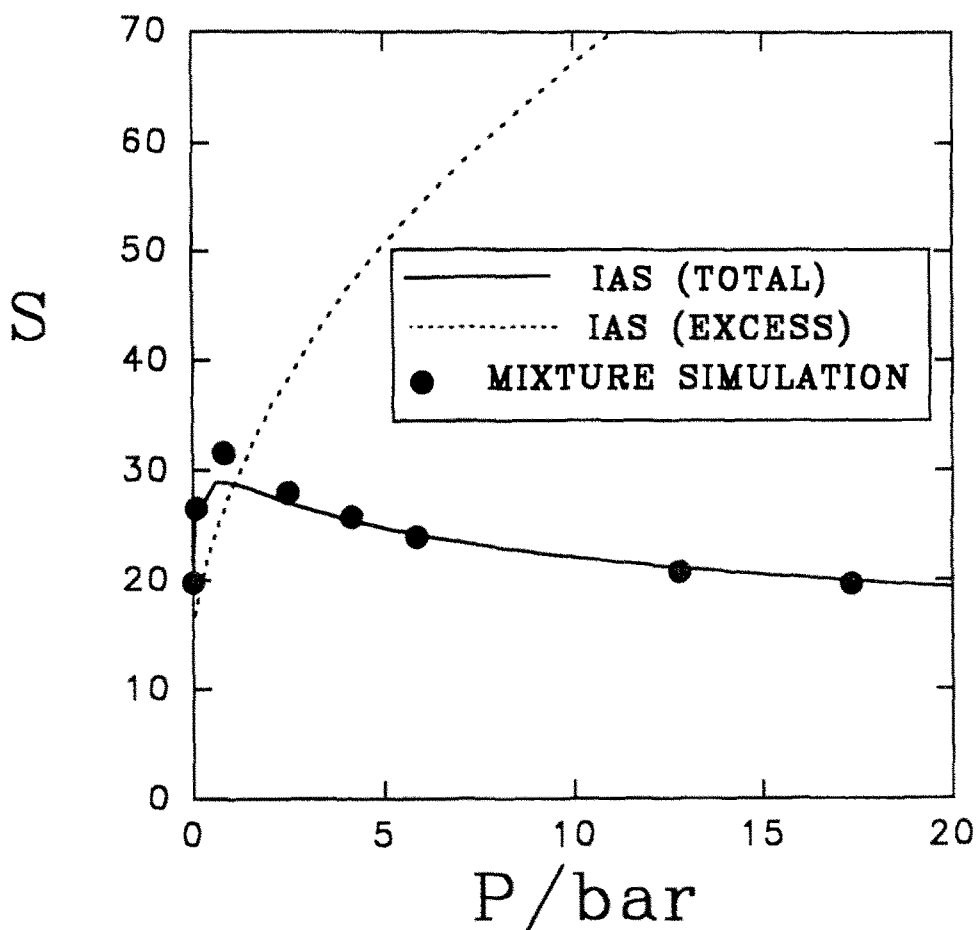


Fig. 5. Selectivity versus pressure. Methane/Ethane mixtures in a slit pore of width, $H = 2.5 \sigma_{\text{CH}_4}$ (0.9525 nm) $T = 296.2$ K. Equimolar bulk gas.

where the IAS appears to fail badly [e.g. for $\text{CO}_2\text{-CH}_4$ in MS 5A (Sievers and Mersmann, 1993)] that this may be at least in part due to using excess isotherms.

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