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On the Azeotropic Behaviour of Adsorption Systems

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Abstract. This paper addresses the azeotropic behaviour of adsorption occurring on a heterogeneous solid, which is composed of patches of different adsorption energies. One of the adsorbates is excluded from adsorption onto one or more patches. If such species is the weaker adsorbing species, then the azeotropic behaviour does not occur. On the other hand, if that species is the stronger adsorbing species then the azeotropic phenomenon *might* occur. The occurrence of the azeotropic depends on the relative affinities of all species and the total pressure must be greater than a threshold pressure. We shall illustrate this theory with two systems exhibiting azeotropic behaviour: isobutane/ethylene/13X and propane/carbon dioxide/mordenite.

Keywords: azeotropic, heterogeneous solid, equilibrium

1. Introduction

Adsorption processes are used more frequently to separate mixtures containing adsorbates of either differing in affinities (equilibrium separation) or differing in the rate of entry into the particle (kinetic separation) (Ruthven, 1984; Yang, 1987). Understanding the equilibria and kinetics of a process is a pre-requisite for better designing an adsorber. For many systems, such a design is relatively straightforward. However, in some systems, the selectivity is not favourable toward any particular species over a range of concentrations, but rather such selectivity switches from one species to another when the compositions are varied. Such a behaviour is known as the azeotropic behaviour, and very often this is treated by assuming a nonideal adsorbed phase (Sircar, 1991) and an introduction of the activity coefficient for that phase.

In this paper, we will address this azeotropic behaviour, and propose a mechanism whereby the azeotropic can be explained by assuming the solid being composed of at least two distinct patches of adsorption sites. If these patches behaves ideally in the sense that the Langmuir assumptions are valid, then the adsorption isotherm will be in the form of dual Langmuir isotherm first proposed by Langmuir (1917). Analysis of such an assumption can lead to many behaviours, and one of such behaviours is the azeotropic phenomenon. We shall derive the various criteria under which the azeotropic behaviour might occur, and will apply such a theory to two systems known for their exhibition of azeotropic behaviour:

1. iso-butane/ethylene/13X by Hyun and Danner (1982),
2. propane/carbon dioxide/mordenite by Talu and Zwiebel (1986).

2. Theory

In this theory, the adsorbed phase is considered to be composed of two patches of adsorption sites. By the term of patch here we do not mean patches of surfaces, but rather in a more general form that the adsorbed phase is composed of two distinct regions, which are assumed to be independent of each other. Adsorption on each patch is direct from the gas phase, and at equilibrium the chemical potential of the gas phase is in equilibrium with those of the two adsorbed phases. Let us assume that the patch 1 has stronger adsorption interaction energy than the patch 2 does, and the solid is exposed to a pure component fluid. The adsorption of the pure component on each patch can be assumed to follow the Langmuir equation. We shall generalise this isotherm equation to the Toth equation to account for the patch heterogeneity later.

There are five possibilities that a system of this type of solid can have:

Case 1. The adsorption on these two sites is progressing with respect to adsorbate affinity, that is the component having stronger affinity in one site will exhibit stronger affinity in the other site.

Case 2. The adsorption on the weaker patch (patch 2) is restricted to the stronger species.

Case 3. The adsorption on the weaker patch is restricted to the weaker species.

Case 4. The adsorption on the stronger patch (patch 1) is restricted to the stronger species.

Case 5. The adsorption on the stronger patch is restricted to the weaker species.

Cases 1, 2 and 4 will never give rise to any azeotropic as the competition of the stronger species is always dominant in both patches. Hence the system is favourable to the stronger species at equilibrium. This will leave the case 3 and case 5 for being possible candidate to give rise to the azeotropic behaviour.

For the cases 3 and 5, we shall consider the two situations whereby the saturation capacities are the same or different for different species in each patch. If the saturation capacities are the same for all species, then the extended Langmuir isotherm equation can be used to describe the capacity of the species "i" under the mixture conditions. If the saturation capacities are different, then we apply the IAS theory (Myers and Prausnitz, 1965) to obtain the capacity for each component under the mixture conditions.

We now first consider the case 3 and will deduce the behaviour of case 5 based on the result of case 3.

2.1. *Adsorption on Weaker Patch Restricted to the Weaker Species (Case 3)*

2.1.1. Langmuir Isotherm. Let us now consider the case 3 where the weaker patch (patch 2) is available to the weaker species. One can visualise this situation as the one where the patch 1 represents the micropore space in a microporous solid while the patch 2 is the region where there are functional groups so that only the weaker species having a property such as dipole to interact with. The stronger species is the one having higher boiling point compared to the weaker one so that it would interact strongly with the surface atoms of the micropore.

To numerically illustrate this case, we study the following three simple examples. We shall denote 1 to the stronger adsorbing species and 2 to the weaker adsorbing species. By "stronger" here we mean that the species 1 has higher affinity towards the patch 1.

Example 1. We choose the following pure component adsorption isotherm equations for the strong and weak adsorbates in the stronger patch 1:

$$C_{\mu 1}^{0} = 2\frac{0.2p}{1+0.2p} \quad (\text{mmol/g}) \tag{1a}$$

$$C_{\mu 2}^{0} = 2\frac{0.08p}{1+0.08p} \quad (\text{mmol/g}) \tag{1b}$$

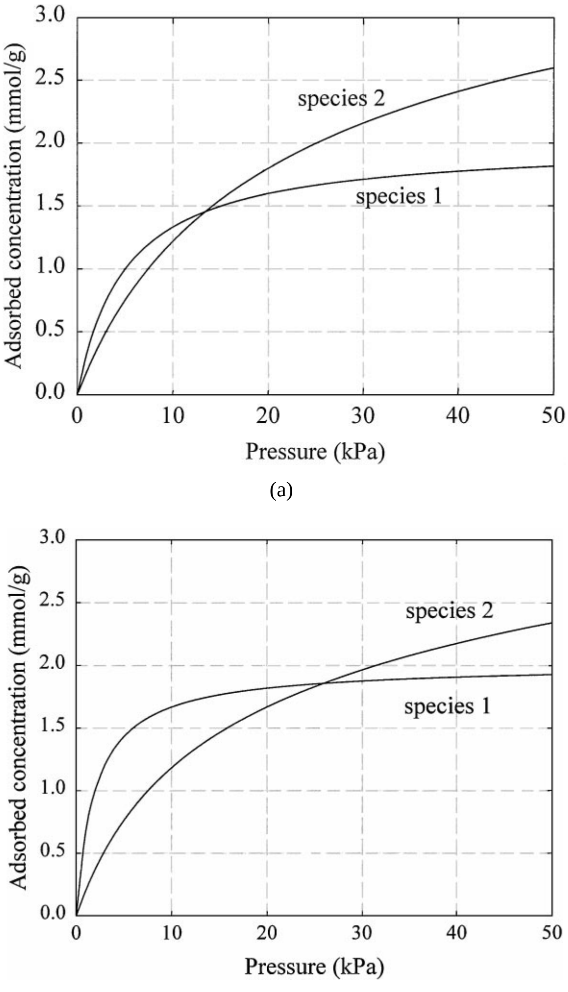
where the saturation capacities of these two species are the same. The affinities of the species 1 and 2 are 0.2 and 0.08 kPa^{-1}, respectively. For this patch, the selectivity of the first species to the second species is 2.5, resulting in a favourable separation towards the first species within this patch:

$$\begin{aligned} S_{12} &= \frac{C_{\mu 1}/p_1}{C_{\mu 2}/p_1} = \frac{2(0.2)/(1+0.2p_1+0.08p_2)}{2(0.08)/(1+0.2p_1+0.08p_2)} \\ &= 2.5 \end{aligned} \tag{2}$$

This is only true for the patch 1, but the solid does contain two patches. Although the patch 2 is weaker than the first patch, it is available only to the weaker component, giving this weak component a possible chance to compete with the stronger species when certain conditions are met. So when the total pressure is reasonably high, the patch-selectivity of the first patch is always maintained at 2.5, and since its saturation capacity is finite, the overall selectivity will depend on the weaker patch as well. Let us now illustrate this point. If we take the adsorption isotherm of the weaker component 2 on the weaker patch 2 is

$$C_{\mu 2}^{0} = 2\frac{0.02p}{1+0.02p} \quad (\text{mmol/g}) \tag{3}$$

Note that the affinity of the component 2 on this weaker patch is smaller than that on the stronger patch 1, which



(a)

(b)

Figure 1. (a) Adsorption isotherm of Example 1; (b) Adsorption isotherm of Example 2.

is 0.08. The adsorption isotherms of the two components are shown in Fig. 1a, where we see that the component 1 is strongly adsorbing (higher Henry constant) at low pressure but has lower capacity at higher pressures. What we also see is the crossing-over of the two adsorption isotherms. This crossing-over has been known to give rise to the azeotropic phenomenon as indicated by Cook and Basmadjian (1965).

Under the mixture conditions of partial pressures p_1 and p_2 in the bulk gas phase, the adsorption capacity of the component 1 is

$$C_{\mu 1} = 2\frac{0.2p_1}{1 + 0.2p_1 + 0.08p_2} \tag{4}$$

while the capacity of the component 2 has two contributions (one from each patch):

$$C_{\mu 2} = 2\frac{0.08p_1}{1 + 0.2p_1 + 0.08p_2} + 2\frac{0.02p_2}{1 + 0.02p_2} \tag{5}$$

This means that the total capacity of two adsorbates on the solid at this mixture condition is

$$C_{\mu \mathrm{T}} = 2\frac{0.2p_1 + 0.08p_1}{1 + 0.2p_1 + 0.08p_2} + 2\frac{0.02p_2}{1 + 0.02p_2} \tag{6}$$

Let x and y be the mole fraction of the component 1 in the adsorbed phase and the gas phase, respectively. We have

$$x = \frac{C_{\mu 1}}{C_{\mu \mathrm{T}}}; \quad y = \frac{p_1}{P}; \quad 1 - y = \frac{p_2}{P} \tag{7}$$

where P is the total pressure. With these definitions, we derive the following relationship between the adsorbed mole fraction and the gas phase mole fraction with the total pressure as the varying parameter.

$$x = \frac{\dfrac{0.2y}{1 + 0.2Py + 0.08P(1-y)}}{\dfrac{0.2y + 0.08(1-y)}{1 + 0.2Py + 0.08P(1-y)} + \dfrac{0.02(1-y)}{1 + 0.02P(1-y)}} \tag{8}$$

Figure 2 shows a plot of the adsorbed phase mole fraction versus the gas phase mole fraction with the total pressure as the varying parameter. We use the following values for the total pressure, 10, 100, 200,

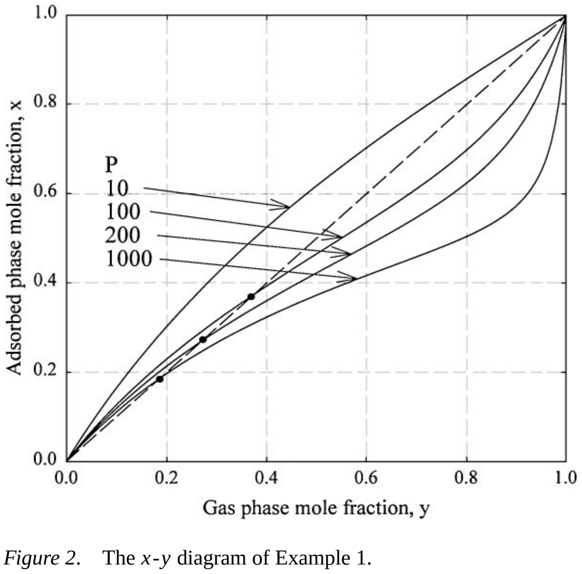
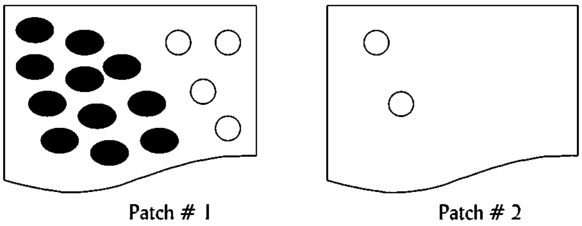


Figure 2. The x-y diagram of Example 1.

(a) Low pressure: Selectivity is favourable toward the stronger species



(b) High pressure: Selectivity is favourable toward the weaker species

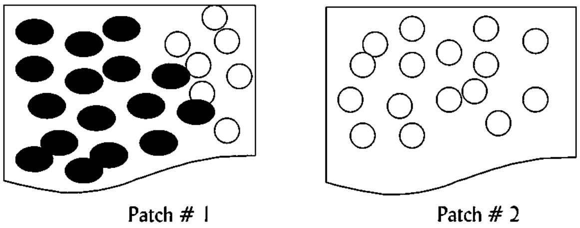


Figure 3. Schematic diagram to illustrate the reversal selectivity.

1000 kPa. What we observe is that at the very low total pressure ($P = 10$ kPa), there is no azeotropic behaviour. This is because at low pressure the patch 2 is not competitive enough to give the weaker species a chance to reverse the patch-selectivity of the patch 1 (which is 2.5), where the stronger species is favourable. Thus the overall selectivity is favourable towards the stronger species. However, when the total pressure is increased to 100 kPa or higher, high enough to give the weaker species an opportunity to reverse the patch-selectivity because of its extra contribution from the weaker patch 2. As a result, we see the azeotropic behaviour, a selectivity reversal, a phenomenon is possible when only the weaker component is accessible to the patch of lower energy.

The following schematic diagram (Fig. 3) shows two situations. In one case the stronger species dominates (Fig. 3a), and in the other the weaker dominates (Fig. 3b). The filled symbol represents the stronger species while the unfilled symbol represents the weaker species. The case (a) is the case of low pressure where the pressure is not high enough for the weaker species in the weaker patch 2 to compete. The other case is that when the pressure is high enough so that the capacity of the weaker species in the weaker patch is now high enough to compete.

Example 2. Let us now choose another combination where the patch 1 has higher adsorption energy than that in the last example and the patch 2 available only to the weaker component has adsorption energy lower than that in the last example. This example represents a solid having *larger variance* in adsorption energy.

Patch 1 The adsorption isotherm equations for the patch 1 are:

$$C^0_{\mu 1} = 2\frac{0.5p}{1 + 0.5p} \quad (\text{mmol/g}) \tag{9a}$$

$$C^0_{\mu 2} = 2\frac{0.1p}{1 + 0.1p} \quad (\text{mmol/g}) \tag{9b}$$

In this example, the affinities of the components 1 and 2 are 0.5 and 0.1 kPa^{-1}, compared to 0.2 and 0.08 in the last example. The saturation capacities are remained the same at 2 mmol/g.

Patch 2 In the second patch, only the weaker component is accessible, and the adsorption isotherm is

$$C^0_{\mu 2} = 2\frac{0.01p}{1 + 0.01p} \tag{10}$$

The adsorption isotherms for the two adsorbates are shown graphically in Fig. 1b. Comparing with Fig. 1a, we see that the solid of example 2 has a wider adsorption energy than that in example 1.

With these isotherm equations for the two patches, the relationship between the adsorbed mole fraction and the gas phase mole fraction is

$$x = \frac{\dfrac{0.5y}{1 + 0.5Py + 0.1P(1-y)}}{\dfrac{0.5y + 0.1(1-y)}{1 + 0.5Py + 0.1P(1-y)} + \dfrac{0.01(1-y)}{1 + 0.01P(1-y)}} \tag{11}$$

The following figure (Fig. 4) shows the plot of x versus y with the total pressure being the varying parameter. What we observe in this figure is that the azeotropic behaviour is *more pronounced.* This is attributed to the difference in the adsorption energies between the two patches.

Example 3. So far we have assumed that the saturation capacities of the two patches are the same. Let us now consider the case where the saturation capacity of the weaker patch is twice as much as that of the stronger site. The affinities are the same as those used in the example 2. We have the following relationship between the adsorbed phase mole fraction and the gas

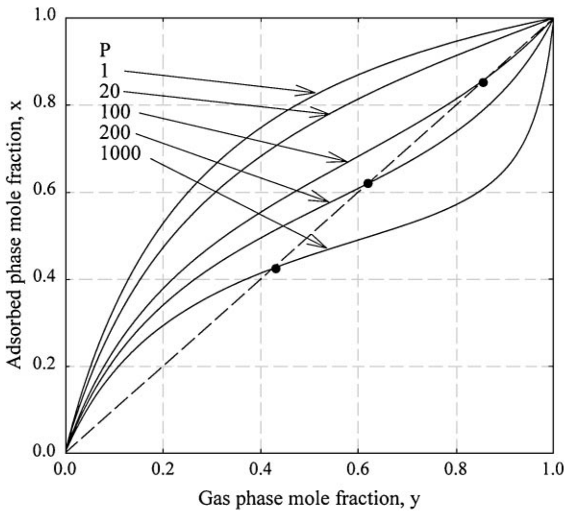


Figure 4. The x-y diagram of Example 2.

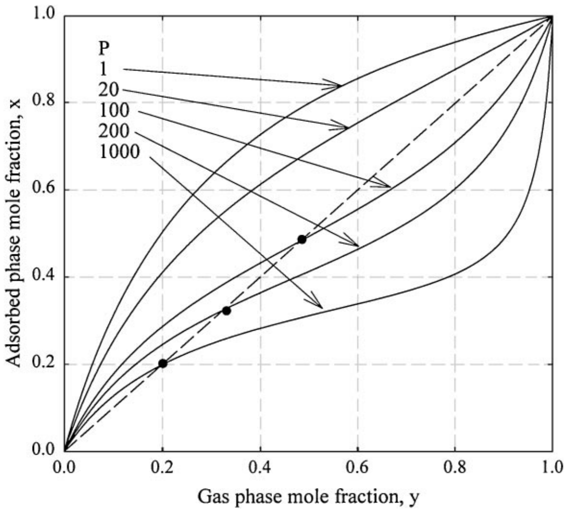


Figure 5. The x-y diagram for the Example 3.

phase mole fraction:

$$x = \frac{\frac{0.5y}{1+0.5Py+0.1P(1-y)}}{\frac{0.5y+0.1(1-y)}{1+0.5Py+0.1P(1-y)} + 2\frac{0.01(1-y)}{1+0.01P(1-y)}} \tag{12}$$

Note the factor 2 in the denominator of the above equation. It is the ratio of the saturation capacity of the patch 2 to that of patch 1. With this example the azeotropic behaviour occurs sooner (Fig. 5) at lower gas phase mole fraction than those in the previous example. This is simply due to the higher contribution of the weaker species by the weaker patch 2.

Thus from the numerical examples thus far, we could summarise the essential behaviour of the azeotropic phenomenon as follows. The azeotropic occurs when the patch of lower interaction energy is available only to the weaker component, and the total pressure is greater than a threshold pressure. The wider is the energy variance of the adsorbed phase, the sharper is the azeotropic on x-y diagram. Also the larger is the ratio of the saturation capacity in the weak patch to that in the stronger patch, the sooner is the selectivity reversal. We will consider in the next section the derivation of quantitative conditions under which the azeotropic behaviour occurs.

2.1.2. Azeotropic Criteria for the Langmuir Isotherm.

To quantify the conditions when the azeotropic would occur, we let b_1^{I} be the adsorption affinity of the strong species on the patch of higher adsorption energy (patch 1), b_2^{I} be that of the weaker species, and b_2^{II} be the adsorption affinity of the weak species on the patch of lower adsorption energy (patch 2). Then the pure component isotherms for these two species in the two patches are

Patch 1 (stronger patch)

$$C_{\mu 1}^{0} = C_{\mu s}^{\mathrm{I}} \frac{b_1^{\mathrm{I}} p}{1 + b_1^{\mathrm{I}} p} \tag{13a}$$

$$C_{\mu 2}^{0} = C_{\mu s}^{\mathrm{I}} \frac{b_2^{\mathrm{I}} p}{1 + b_2^{\mathrm{I}} p} \tag{13b}$$

Patch 2 (weaker patch)

$$C_{\mu 2}^{0} = C_{\mu s}^{\mathrm{II}} \frac{b_2^{\mathrm{II}} p}{1 + b_2^{\mathrm{II}} p} \tag{13c}$$

With these isotherm expressions, the relationship between the mole fraction in the adsorbed phase to that of the gas phase is

$$x = \frac{\frac{b_1^{\mathrm{I}} y}{1+b_1^{\mathrm{I}} Py + b_2^{\mathrm{I}} P(1-y)}}{\frac{b_1^{\mathrm{I}} y + b_2^{\mathrm{I}}(1-y)}{1+b_1^{\mathrm{I}} Py + b_2^{\mathrm{I}} P(1-y)} + \alpha \frac{b_2^{\mathrm{II}}(1-y)}{1+b_2^{\mathrm{II}} P(1-y)}} \tag{14a}$$

where α is the ratio of the saturation capacities of the weaker patch to the stronger patch, i.e.

$$\alpha = \frac{C_{\mu s}^{\mathrm{II}}}{C_{\mu s}^{\mathrm{I}}} \tag{14b}$$

If the y-x curve cuts the 45° line, then the following equation must be true:

$$y = \frac{\dfrac{b_1^{\mathrm{I}} y}{1 + b_1^{\mathrm{I}} P y + b_2^{\mathrm{I}} P(1-y)}}{\dfrac{b_1^{\mathrm{I}} y + b_2^{\mathrm{I}}(1-y)}{1 + b_1^{\mathrm{I}} P y + b_2^{\mathrm{I}} P(1-y)} + \alpha \dfrac{b_2^{\mathrm{II}}(1-y)}{1 + b_2^{\mathrm{II}} P(1-y)}} \tag{15}$$

Solving for y, we get:

$$y = \frac{\left(b_1^{\mathrm{I}} - b_2^{\mathrm{I}}\right)\left(1 + b_2^{\mathrm{II}} P\right) - \alpha b_2^{\mathrm{II}}\left(1 + b_2^{\mathrm{I}} P\right)}{(1+\alpha)\left(b_1^{\mathrm{I}} - b_2^{\mathrm{I}}\right) b_2^{\mathrm{II}} P} \tag{16}$$

For this solution to occur within the physical limit, we must have $y < 1$, that is the constraint for the total pressure is

$$P > \frac{\left(b_1^{\mathrm{I}} - b_2^{\mathrm{I}}\right) - \alpha b_2^{\mathrm{II}}}{\alpha b_1^{\mathrm{I}} b_2^{\mathrm{II}}} \tag{17}$$

For example, we use the parameters used in the example 3, $b_1^{\mathrm{I}} = 0.5$, $b_2^{\mathrm{I}} = 0.1$ and $b_2^{\mathrm{II}} = 0.01$ kPa^{-1} and $\alpha = 2$, the constraint on the total pressure for the azeotropic to occur is

$$P > 38 \text{ kPa}$$

Using the above equation, we can deduce the conditions of the system such that the azeotropic exists so that $P > 0$, that is

$$\left(b_1^{\mathrm{I}} - b_2^{\mathrm{I}}\right) - \alpha b_2^{\mathrm{II}} > 0 \tag{18a}$$

or

$$b_1^{\mathrm{I}} > b_2^{\mathrm{I}} + \alpha b_2^{\mathrm{II}} \tag{18b}$$

Since α is the ratio of the two saturation capacities, the above equation can be rewritten as:

$$C_{\mu s}^{\mathrm{I}} b_1^{\mathrm{I}} > C_{\mu s}^{\mathrm{I}} b_2^{\mathrm{I}} + C_{\mu s}^{\mathrm{II}} b_2^{\mathrm{II}} \tag{19a}$$

which simply states that the Henry constant of the stronger species must be greater than the Henry constant of the other species, which is the sum of the two Henry constants of the two patches, i.e.

$$K_1^{\mathrm{I}} > K_2^{\mathrm{I}} + K_2^{\mathrm{II}} \tag{19b}$$

Thus the conditions necessary for the azeotropic to occur are:

(i) $b_1^{\mathrm{I}} > b_2^{\mathrm{I}} + \alpha b_2^{\mathrm{II}}$ or $K_1^{\mathrm{I}} > K_2^{\mathrm{I}} + K_2^{\mathrm{II}}$ (20a)

(ii) $C_{\mu s}$ (weaker species) $> C_{\mu s}$ (stronger species) (20b)

(iii) $$P > P_{\text{threshold}} = \frac{\left(b_1^{\mathrm{I}} - b_2^{\mathrm{I}}\right) - \alpha b_2^{\mathrm{II}}}{\alpha b_1^{\mathrm{I}} b_2^{\mathrm{II}}} \tag{20c}$$

The conditions (20a) and (20b) represent the situation where the adsorption isotherms of the strong and weak species cross over each other. This has been suggested by Cook and Basmadjian (1965), but no criteria were derived for the necessary existence of azeotropic. The threshold pressure above which the azeotropic occurs is given in Eq. (20c).

When these conditions (Eq. 20) are satisfied the gas phase mole fraction at which the selectivity reversal occurs is:

$$y = \frac{\left(b_1^{\mathrm{I}} - b_2^{\mathrm{I}}\right)\left(1 + b_2^{\mathrm{II}} P\right) - \alpha b_2^{\mathrm{II}}\left(1 + b_2^{\mathrm{I}} P\right)}{(1+\alpha)\left(b_1^{\mathrm{I}} - b_2^{\mathrm{I}}\right) b_2^{\mathrm{II}} P} \tag{21}$$

Let us illustrate this further by considering three examples based on the relative magnitude of the azeotropic behaviour condition (i) (Eq. (20a)).

Without loss of generality, we choose $\alpha = 2$ for examples 4–6.

Example 4 ($b_1^{\mathrm{I}} < b_2^{\mathrm{I}} + \alpha b_2^{\mathrm{II}}$). With the values $b_1^{\mathrm{I}} = 0.5$; $b_2^{\mathrm{I}} = 0.3$; $b_2^{\mathrm{II}} = 0.2$, we have $b_1^{\mathrm{I}} < b_2^{\mathrm{I}} + \alpha b_2^{\mathrm{II}}$. This is the case where the species 1 is stronger than the species 2 within the patch 1, but with the patch 2 included the species 2 has a higher Henry constant than the other species. The following figure (Fig. 6) shows the plot of the adsorbed mole fraction versus the gas phase mole fraction. The solid is favourable to the species 2 because its overall Henry constant is larger than that of the species 1 although it has lower affinity within the patch 1.

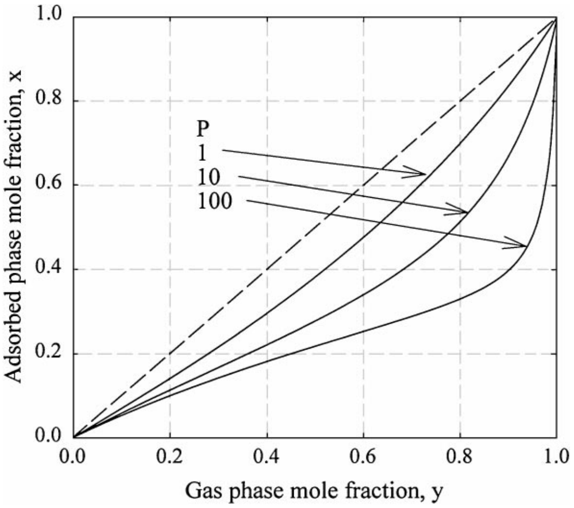


Figure 6. The x-y diagram of Example 4.

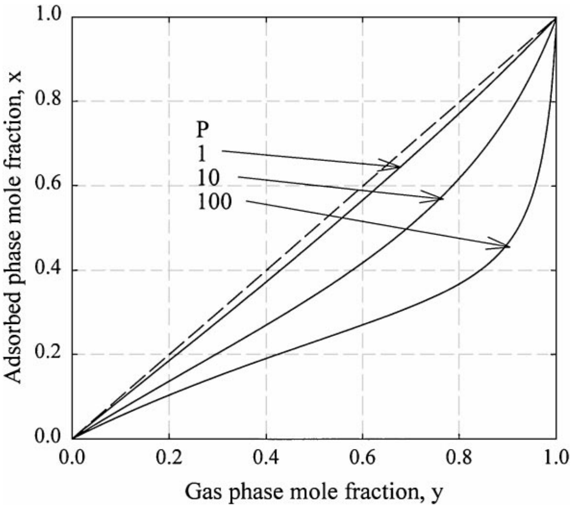


Figure 7. The x-y diagram of Example 5.

Example 5 ($b_1^{\mathrm{I}} = b_2^{\mathrm{I}} + \alpha b_2^{\mathrm{II}}$). With the values $b_1^{\mathrm{I}} = 0.5$; $b_2^{\mathrm{I}} = 0.3$; $b_2^{\mathrm{II}} = 0.1$, we have $b_1^{\mathrm{I}} = b_2^{\mathrm{I}} + \alpha b_2^{\mathrm{II}}$. The following figure (Fig. 7) shows the plot of the adsorbed mole fraction versus the gas phase mole fraction. No azeotropic occurs because the threshold pressure for this choice of parameters is zero. The solid is preferential towards the species 2.

Example 6 ($b_1^{\mathrm{I}} > b_2^{\mathrm{I}} + \alpha b_2^{\mathrm{II}}$). With the values $b_1^{\mathrm{I}} = 0.5$; $b_2^{\mathrm{I}} = 0.1$; $b_2^{\mathrm{II}} = 0.02$, we have $b_1^{\mathrm{I}} > b_2^{\mathrm{I}} + \alpha b_2^{\mathrm{II}}$. The following figure (Fig. 8) shows the plot of the adsorbed mole fraction versus the gas phase mole fraction. This type of behaviour has been observed in simulation examples 1 to 3.

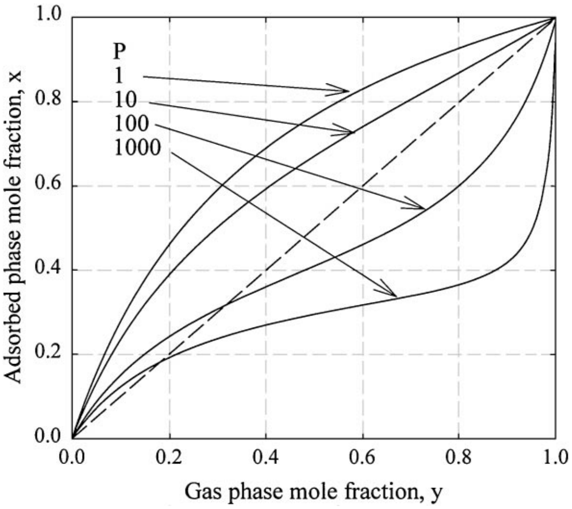


Figure 8. The x-y diagram of Example 6.

2.1.3. Toth Isotherm. The analysis in the last section is based on the Langmuir isotherm on each patch and the saturation capacities of different species are the same on each patch. This is sufficient to bring out the essential features of the azeotropic behaviour as well as the conditions for the azeotropic to occur. In practice the Langmuir equation usually does not describe the data well and for such cases we shall consider in this section the Toth equation for the description of adsorption data, that is the isotherm equation for the stronger species on the stronger patch 1 is

$$C_{\mu 1}^{\mathrm{I}} = C_{\mu s1}^{\mathrm{I}} \frac{b_1^{\mathrm{I}} P}{\left[1 + \left(b_1^{\mathrm{I}} P\right)^{t_1}\right]^{1/t_1}} \tag{22a}$$

Similarly the isotherm equation for the weaker species in the patch 1 is

$$C_{\mu 2}^{\mathrm{I}} = C_{\mu s2}^{\mathrm{I}} \frac{b_2^{\mathrm{I}} P}{\left[1 + \left(b_2^{\mathrm{I}} P\right)^{t_2}\right]^{1/t_2}} \tag{22b}$$

The isotherm equation for the weaker species in the patch 2 is

$$C_{\mu 2}^{\mathrm{II}} = C_{\mu s2}^{\mathrm{II}} \frac{b_2^{\mathrm{II}} P}{\left[1 + \left(b_2^{\mathrm{II}} P\right)^{t_2^{\mathrm{II}}}\right]^{1/t_2^{\mathrm{II}}}} \tag{22c}$$

Under the mixture conditions, the adsorbed concentration for the patch 2 is given as in Eq. (22c) because only the species 2 can access to that patch. For patch 1, we use the IAS theory (Myers and Prausnitz, 1965) to calculate the adsorbed concentration for the mixture. The mole fraction of the species 1 in the adsorbed phase is then

$$x = \frac{C_{\mu 1}^{\mathrm{I}}}{C_{\mu 1}^{\mathrm{I}} + C_{\mu 2}^{\mathrm{I}} + C_{\mu 2}^{\mathrm{II}}} \tag{23}$$

2.1.4. Iso-butane/Ethylene/13X. We test this with the experimental data of iso-butane(1)/ethylene(2)/13X zeolite of Hyun and Danner (1981). Let us assume that the zeolite 13X has micropore channels where both ethylene and iso-butane can compete and a patch of sites where only the ethylene can interact with. Using the Toth equation to fit the pure component data of iso-butane, we get

$$C_{\mu 1}^{\mathrm{I}} = 2.1246 \frac{162.6P}{[1 + (162.6P)^{0.3168}]^{1/0.3168}} \tag{24}$$

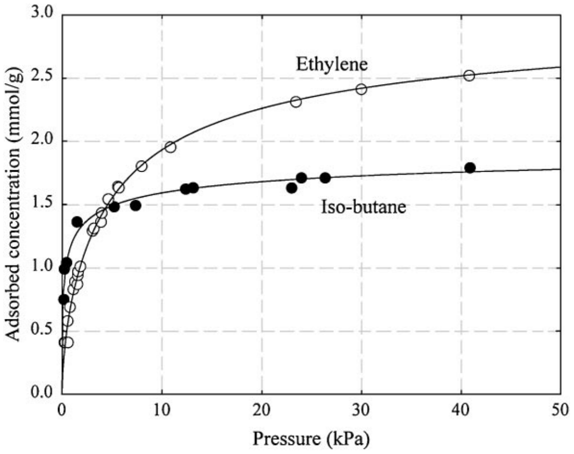


Figure 9. The adsorption isotherms of iso-butane (1) and ethylene (2) on 13X zeolite.

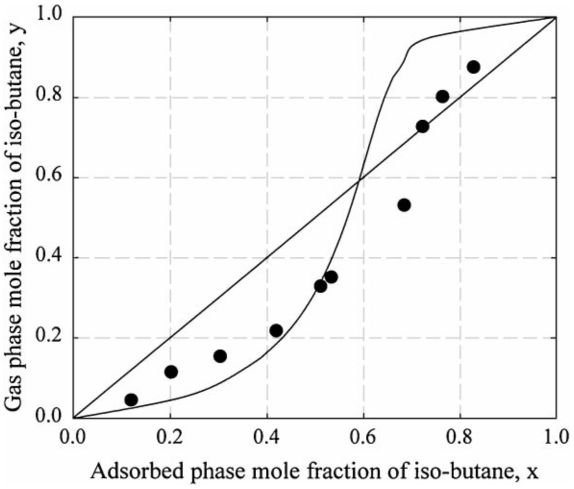


Figure 10. Plot of the gas phase mole fraction versus the adsorbed phase mole fraction of iso-butane.

On the other hand, using the dual Toth equation to fit the data of ethylene, we obtain

$$C_{\mu 2} = 2.375 \frac{2.383P}{[1 + (2.383P)^{0.383}]^{1/0.383}} + 1.053 \frac{0.181P}{[1 + (0.181P)^{1.117}]^{1/1.117}} \quad (25)$$

The adsorption data as well as the fitted curves (24) and (25) for iso-butane and ethylene are shown in Fig. 9. We see that the two isotherms cross each other at about 5 kPa, with isobutane having higher overall Henry constant than ethylene.

The first term in the RHS of Eq. (25) for ethylene is associated with the patch 1 where the stronger adsorbing component, iso-butane, also adsorbs. Using the IAS on the first patch, we obtain the adsorbed concentration for iso-butane and ethylene under the mixture conditions. The ethylene adsorbed concentration on the patch 2 is simply calculated from the second term of Eq. (25). A plot of the gas phase mole fraction versus the adsorbed phase mole fraction is shown in Fig. 10 for a total pressure of 137.8 kPa and a temperature of 298 K, and the experimental data of Hyun and Danner are also shown as symbols. The predictions from the model generally agree with the experimental data although the point at which the selectivity reversal predicted by the model occurs at a gas phase mole fraction of 0.6 while the experimental data is 0.7. Nevertheless the model is able to explain the existence of the azeotropic behaviour.

2.1.5. Propane/Carbon Dioxide/Mordenite. We now test the theory with the data of propane and carbon dioxide on mordenite (Talu and Zwiebel, 1986) at 303 K and a total pressure of 40.93 kPa. The data of these two compounds are shown in Fig. 11. We note that propane has higher Henry constant while carbon dioxide has higher saturation capacity. The mordenite zeolite is assumed to consist of two regions of adsorbed phase. Carbon dioxide is assumed to adsorb onto both regions, while propane adsorbs only the strong region.

First we fit the propane data with the Toth equation since we assume that propane only adsorbs onto one

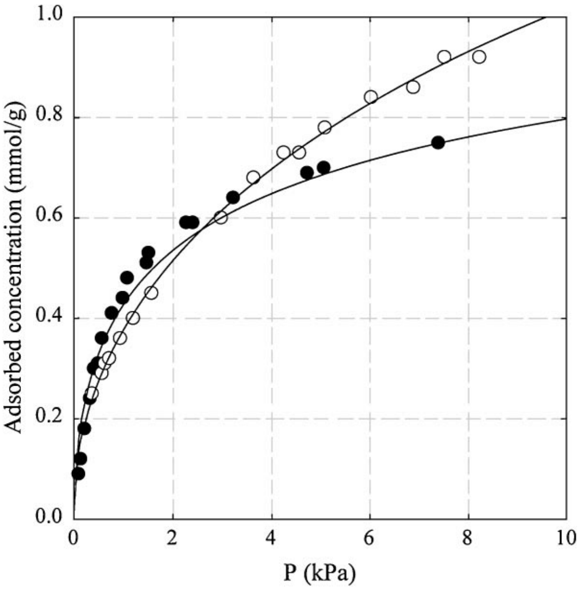


Figure 11. Adsorption isotherms of propane and carbon dioxide on mordenite.

patch. Knowing the adsorption saturation capacity of propane of this patch, we will assume that the saturation capacity on the same patch for carbon dioxide will follow the following equation:

$$\frac{C^{\mathrm{I}}_{\mu s,\text{carbon dioxide}}}{C^{\mathrm{I}}_{\mu s,\text{propane}}} = \left(\frac{\sigma_{\text{carbon dioxide}}}{\sigma_{\text{propane}}}\right)^{-D} \tag{26}$$

where σ is the molecular dimension of the adsorbate, and D is the fractal dimension of the patch 1, which is taken as 2.5 in this work (Keller, 1990).

Fitting the Toth equation

$$C^{\mathrm{I}}_{\mu,\text{propane}} = C^{\mathrm{I}}_{\mu s,\text{propane}} \frac{b^{\mathrm{I}}_{\text{propane}}\, p}{\left[1+\left(b^{\mathrm{I}}_{\text{propane}}\, p\right)^{t_{\text{propane}}}\right]^{1/t_{\text{propane}}}} \tag{27}$$

against the propane data, we get the following optimal parameters: $C^{\mathrm{I}}_{\mu s,\text{propane}} = 1.535$ mmol/g; $b^{\mathrm{I}}_{\text{propane}} = 5.782$; $t^{\mathrm{I}}_{\text{propane}} = 0.3413$.

With the above saturation capacity for propane, we use Eq. (26) with $\sigma_{\text{propane}} = 5.061$ A and $\sigma_{\text{carbon dioxide}} = 3.996$ A (Bird et al., 1960) to calculate the saturation capacity for carbon dioxide in the patch 1, which is $C^{\mathrm{I}}_{\mu s,\mathrm{CO_2}} = 2.7713$ mmol/g.

The overall isotherm of carbon dioxide is assumed to be a combination of the two Toth equations, one for each patch, which is

$$\begin{aligned} C_{\mu,\mathrm{CO_2}} = {} & C^{\mathrm{I}}_{\mu s,\mathrm{CO_2}} \frac{b^{\mathrm{I}}_{\mathrm{CO_2}}\, p}{\left[1+\left(b^{\mathrm{I}}_{\mathrm{CO_2}}\, p\right)^{t^{\mathrm{I}}_{\mathrm{CO_2}}}\right]^{1/t^{\mathrm{I}}_{\mathrm{CO_2}}}} \\ & + C^{\mathrm{II}}_{\mu s,\mathrm{CO_2}} \frac{b^{\mathrm{II}}_{\mathrm{CO_2}}\, p}{\left[1+\left(b^{\mathrm{II}}_{\mathrm{CO_2}}\, p\right)^{t^{\mathrm{II}}_{\mathrm{CO_2}}}\right]^{1/t^{\mathrm{II}}_{\mathrm{CO_2}}}} \end{aligned} \tag{28}$$

Using the calculated saturation capacity for the patch 1 (2.7713 mmol/g), we fit the above equations with the experimental data of $\mathrm{CO_2}$ to obtain the following:

$$\begin{aligned} C_{\mu,\mathrm{CO_2}} = {} & 2.7713 \frac{365.86p}{[1+(365.86p)^{0.1426}]^{1/0.1426}} \\ & + 4.1833 \frac{0.0982p}{[1+(0.0982p)^{0.359}]^{1/0.359}} \end{aligned} \tag{29}$$

The first term is for the patch 1, while the second term is for patch 2.

For the mixtures, the adsorption capacity of the first term of the above equation for $\mathrm{CO_2}$ competes with that for propane in the patch 1. Using the IAS calculation for the adsorbed concentrations in the patch 1, and the second term of the above equation for the patch 2, we calculate the mole fraction of propane in the adsorbed phase as a function of the gas phase mole fraction as shown in Fig. 12 for a total pressure of 40.93 kPa and a temperature of 303 K.

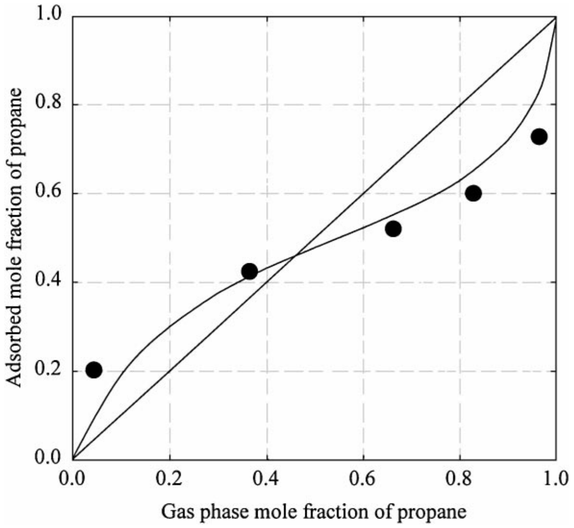


Figure 12. Plot of the gas phase mole fraction versus the adsorbed phase mole fraction of propane.

We see that the predictions from the theory agree very well with the binary experimental data of Talu and Zweibel (1986). Staudt et al. (1995) used a generalised Langmuir-Freundlich equation to also describe the azeotropic behaviour of propane/carbon dioxide/mordenite data, but the analysis does not reveal the mechanism behind the azeotropic. The theory in this paper argues that the presence of two patches in the adsorbed phase and one patch accessible only to the weaker species are responsible for the occurrence of the selectivity reversal, that is the azeotropic behaviour.

2.2. *Adsorption on the Stronger Patch Restricted to the Weaker Species (Case 5)*

This case is the opposite of the case 3. Here the stronger patch is available only to the weaker species. If we assume that the patch 2 is the stronger patch, the analysis for the Langmuir isotherm in section 2.1.2 is applicable and the condition for the azeotropic to occur is:

$$b^{\mathrm{I}}_{1} > b^{\mathrm{I}}_{2} + \alpha b^{\mathrm{II}}_{2} \tag{30a}$$

or

$$C^{\mathrm{I}}_{\mu s} b^{\mathrm{I}}_{1} > C^{\mathrm{I}}_{\mu s} b^{\mathrm{I}}_{2} + C^{\mathrm{II}}_{\mu s} b^{\mathrm{II}}_{2} \tag{30b}$$

One situation where this case could apply is the solid having a range of micropores, and smaller micropores are only accessible to smaller sized adsorbate, which is usually the weaker adsorbing species. Myers (1988) presented a theory of micropore exclusion and he has shown that the existence of this exclusion can give rise to the azeotropic behaviour. Studies of this size exclusion on zeolitic system were studied by Dunnes and Myers (1994).

Let us take the following example to illustrate this case 5.

Patch 1 (weaker patch)

$$b_1^{\mathrm{I}} = 0.5$$
$$b_2^{\mathrm{I}} = 0.1$$

Patch 2 (stronger patch)

$$b_2^{\mathrm{II}} = 0.3$$
$$\alpha = 1$$

With these values, the condition (30a) is satisfied, and we expect the azeotropic will occur when the total pressure is greater than the following threshold pressure:

$$P^* = \frac{\left(b_1^{\mathrm{I}} - b_2^{\mathrm{I}}\right) - \alpha b_2^{\mathrm{II}}}{\alpha b_2^{\mathrm{I}} b_2^{\mathrm{II}}} \tag{31}$$

Figure 13 shows the adsorption isotherm of the two adsorbates.

The x-y diagram for this situation is shown in Fig. 14.

We see that the azeotropic behaviour of the case 5 is different from that of the case 3. In this case the xy curves of different total pressures cross each other, and when the pressure is increased, the point at which the reversal in selectivity occurs decreases and reaches a constant value. The azeotropic occurs more readily in the case 5 than the case 3. This is because only weaker species is accessible to the stronger patch, giving it a better chance to compete with the stronger species.

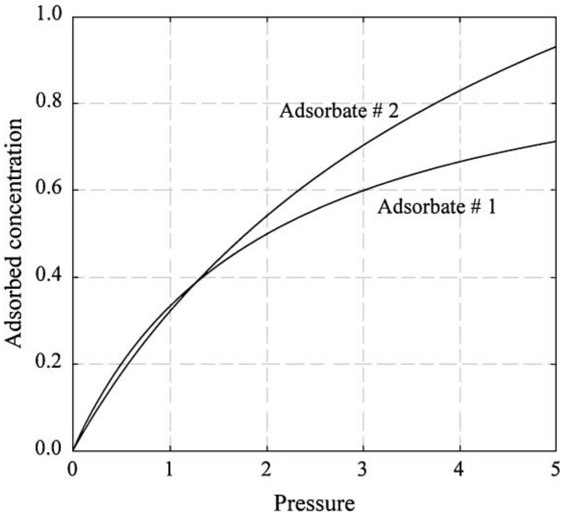


Figure 13. Adsorption isotherms used in case 5.

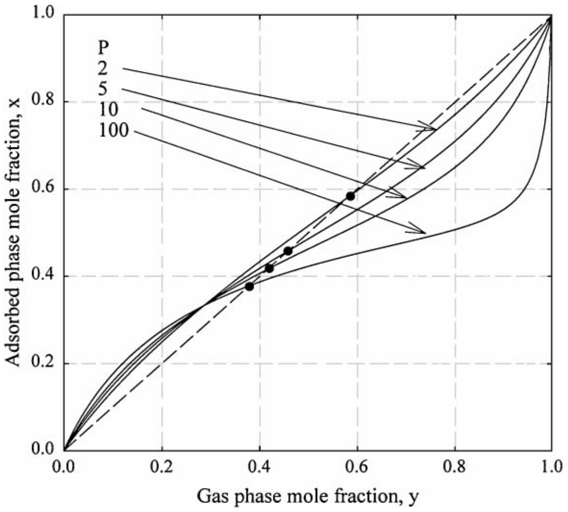


Figure 14. The x-y diagram of case 5.

3. Conclusions

We have presented in this paper a possible explanation for the azeotropic behaviour. Solids having two patches of adsorption sites, and if one of those patches is only accessible to the weaker species then azeotropic might occur. The necessary conditions for the azeotropic are that the Eq. (20a,b) is satisfied and the pressure is greater than a threshold pressure given by Eq. (20c). Two systems of isobutane/ethylene/13X and propane/carbon dioxide/mordenite are tested to illustrate the concept of this theory.

Nomenclature

b	Adsorption affinity, kPa^{-1}
C_μ	Adsorbed concentration, mmol/g
$C_{\mu\mathrm{s}}$	Saturation capacity, mmol/g
$C_{\mu\mathrm{T}}$	Total adsorbed concentration, mmol/g
K	Henry constant, $=bC_{\mu\mathrm{s}}$
p	Partial pressure, kPa
P	Total pressure, kPa
P^*	Threshold pressure, kPa
S_{12}	Selectivity of component 1 to component 2
t	Toth constant

x	Adsorbed phase mole fraction
y	Gas phase mole fraction

Greek Symbols

α	Ratio of saturation capacity of patch 2 to patch 1 (Eq. 14b)
π	Reduced spreading pressure, mmol/g
σ	Molecular diameter, A

Subscript

1, 2	Components 1, 2

Superscript

I, II	Patches 1, 2

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