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Determination of Azeotropic Behavior in Adsorbed Mixtures

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Abstract. An analogy between vapor adsorbed equilibrium and vapor liquid equilibrium is made to determine the condition where azeotropes are observed, using a relationship between infinite dilution activity coefficients and pure component pressures in the reference state. The range of conditions where azeotropic behavior is expected in vapor-adsorbed equilibrium (VAE) was determined for the multisite Langmuir model for a mixture of two components with molecules of different size, and for CO_2-C_3H_8 on NaX using an empirical model (Siperstein and Myers, 2001), which has been shown to correlate accurately experimental data.

Keywords: azeotrope, mixture, thermodynamics

1. Introduction

Understanding the behavior of nonideal adsorbed mixtures is of great industrial importance. In particular, the determination of the existence of azeotropes is crucial for the design of adsorption separation equipment. Studies focusing on causes of nonideal behavior, such as different adsorbate sizes, lateral interactions between adsorbed molecules, partial exclusion of one adsorbate from some regions of the adsorbent and adsorbent heterogeneity are available in the literature (see for example: Sircar, 1995; Kaminski and Monson, 1993; Ritter and Al-Muhtaseb, 1998).

The ideal adsorbed solution (IAS) theory or the mixed Langmuir model are unable to show the formation of azeotropes. However, extensions of these models, such as the heterogeneous ideal adsorbed solution (HIAS) (Valenzuela et al., 1988) or the multisite Langmuir model (Nitta et al., 1984) can predict the formation of azeotropes.

One of the most studied phenomenon that can produce adsorbed azeotropes are excluded volume effects. In these cases, the change in energy due to the adsorption of large molecules is usually bigger than for small molecules. Therefore, adsorption of large molecules is favored at low densities. For high densities, adsorption of the small molecules can be more favorable because they can occupy space that is not accessible for the large molecules (Dunne and Myers, 1994).

Adsorption of mixtures of molecules, where the main difference between the components is the size of the adsorbate, is characterized by isotherms that cross at some particular pressure. The multisite Langmuir model, as well as other extensions of the Langmuir model are able to produce azeotropic behavior for mixtures of adsorbates of different size, and at pressures above the crossing point of the pure component isotherms (Sircar, 1995; Martinez and Basmadjian, 1996; Bai and Yang, 2001). At pressures much higher than the point where isotherms cross, complete reversal in selectivity over the whole range of compositions can be observed. The reversal in selectivity with pressure is a phenomenon that has been also observed in molecular simulations (Van Tassel et al., 1994; Keffer et al., 1996). This indicates that the range of conditions where an azeotrope is observed due to size effects is limited.

Most of the Langmuir based models require that single component isotherms cross at some point in order to observe the formation of azeotropes. In the model developed by Ritter and Al-Muhtaseb (1998), crossing of single component isotherms is a necessary but not sufficient condition for formation of azeotropic mixtures. Nevertheless, in some cases it is possible to observe the formation of azeotropes without crossing of the single component isotherms (Siperstein and Myers, 2001).

The present work is oriented towards the determination of the range of conditions where azeotropic behavior is observed in vapor-adsorbed equilibrium (VAE) for Langmuir type models where nonideal behavior is considered. Results from these models are compared to the conditions where azeotropic behavior is expected when using an empirical model (Siperstein and Myers, 2001), which has been shown to correlate accurately experimental data, is also presented. The objective is not to correlate existing experimental data on highly nonideal mixtures, but to provide some guidelines to determine whether or not a mixture will show azeotropic behavior, and in which range of conditions this behavior is expected.

2. Thermodynamic Background

It is possible to make many analogies between VAE and vapor-liquid equilibrium (VLE). For example, the total pressure of a system containing a mixture of gases in equilibrium with an adsorbed phase (or a liquid) can be written as:

$$P = \sum_i p_i^\circ x_i \gamma_i \tag{1}$$

where P is the total pressure, and x_i is the mole fraction of component i in the adsorbed phase for VAE, or the liquid phase for VLE. For VLE, p_i^o is the pure component vapor pressure and γ_i is the liquid phase activity coefficient of component i, both at the same temperature of the mixture. For VAE, p_i^o is the pure component pressure and γ_i is the adsorbed phase activity coefficient of component i, both at the same temperature and surface potential (or spreading pressure) than the mixture (Myers and Prausnitz, 1965; Myers, 2002). The surface potential, Φ, for a pure component is defined as:

$$\Phi = -RT \int_0^P \frac{n}{f} df \tag{2}$$

where n is the amount adsorbed, and f is the fugacity of the adsorbate. For an ideal gas, the fugacity is equal to the pressure. For a mixture with i components, the surface potential is defined as:

$$-\frac{\Phi}{RT} = \sum \int_0^P \frac{n_i}{f_i} df_i \tag{3}$$

where the integrals need to be carried out following a consistent path. The term Φ/RT appears frequently, and it is convenient to define the function ψ, as $\psi = -\Phi/RT$.

In this work, the discussion will be restricted to binary mixtures, although it can be extended to multicomponent systems. The convention used is that component 1 is the strongly adsorbed component at the limit of zero pressure. It follows that at low surface potential, $p_2^o > p_1^o$. When isotherms of both components in a mixture cross at some point, $p_2^o = p_1^o$. Therefore, it is possible to observe, $p_2^o > p_1^o$ at low coverage, but $p_2^o < p_1^o$ at high coverage for mixtures of molecules with different sizes.

The existence of an azeotrope in VLE can be determined from relations between the infinite dilution activity coefficients and the vapor pressure of the pure components at the same temperature than the mixture. These relationships can be obtained from the slope of the bubble point pressure curve as it approaches the pure component. For example, for $p_2^o > p_1^o$, negative azeotrope is observed when

$$\lim_{x_1 \to 1} \frac{dP}{dx_1} > 0 \tag{4}$$

Equations (1) and (4) yield that a negative azeotrope is observed when $\gamma_2^\infty < p_1^o/p_2^o$, where γ_2^∞ is the infinite dilution activity coefficient of component 2. Similar expression for the existence of azeotropes in VAE can be derived considering that the standard state is given by the temperature and surface potential of the mixture.

The condition for observing a negative azeotrope at a given temperature and surface potential should consider whether p_1^o is larger or smaller than p_2^o. In general, the condition for observing an azeotrope at a given temperature and surface potential is given by:

$$\begin{aligned} \gamma_1^\infty &< \frac{p_2^o}{p_1^o} \quad \text{for } p_2^o < p_1^o \\ \gamma_2^\infty &< \frac{p_1^o}{p_2^o} \quad \text{for } p_2^o > p_1^o \end{aligned} \tag{5}$$

These conditions can be evaluated either by using an analytical expression for the activity coefficients and taking the infinite dilution limit, or by using a model for VAE that relates the amount adsorbed and composition inside the pores to the pressure and bulk phase composition.

3. Results and Discussion

Adsorption isotherms of pure components and mixture properties were determined for an idealized case using the multisite Langmuir model. Details of the model used can be found elsewhere (Nitta et al., 1994). The pure component isotherms and the surface potential, ψ, are described by the following equations:

$$P = \frac{\theta}{k(1-\theta)^a} \tag{6}$$

$$\psi = -m[(a-1)\theta + a\ln(1-\theta)] \tag{7}$$

where P is the total pressure, θ is the fractional coverage, m is the saturation capacity, and a is the number of sites occupied by a pure component in the adsorbed phase and k is the Henry's Law constant. For mixture adsorption, the individual fractional coverage is given by:

$$\theta_i = k_i P y_i \left(1 - \sum_j \theta_j\right)^{a_i} \tag{8}$$

where θ_i is the fractional coverage of component i in the adsorbed phase ($\theta_i = n_i/m_i$) and y_i is the gas phase mole fraction. In this work, a simple set of parameters for the multisite Langmuir model have been used to determine the range of conditions where azeotropic behavior is observed. The parameters used are summarized in Table 1, and the pure component adsorption isotherms are shown in Fig. 1. The pure component isotherms cross at an approximate pressure of 6 kPa and a loading of 0.9 mol/kg. For comparison, Fig. 2 shows the surface potential as a function of pressure. It can be seen that the pure component lines cross at a pressure of 35 kPa and a surface potential of 3.6 mol/kg.

At a given value of surface potential, it is possible to calculate the infinite dilution activity coefficient, by comparing the model output with the predictions of the IAS. The infinite dilution activity coefficients start with a value of unity for zero pressure (ideal solution), and they decrease their value as pressure increases (negative

Table 1. Parameters for the multisite Langmuir model.

	Component 1	Component 2
m (mol/kg)	1	2
a	1	0.5
k (kPa^{-1})	10	1

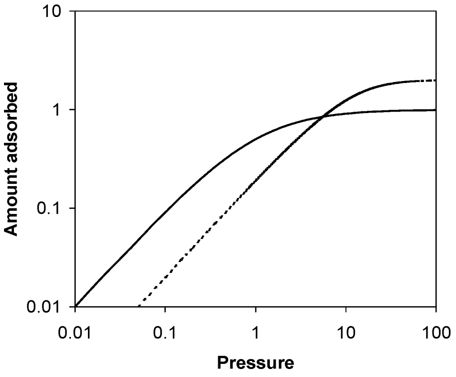


Figure 1. Adsorption isotherms for unequal size adsorbates using the multisite Langmuir model. Solid line is for the strongly adsorbed component and dotted line for the weakly adsorbed component.

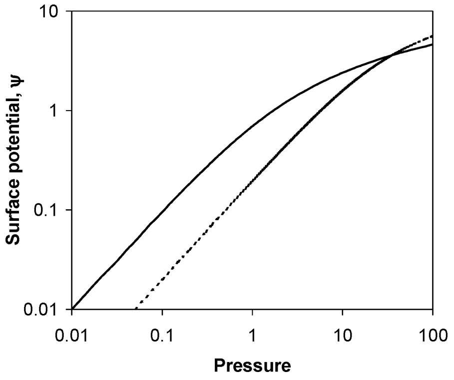


Figure 2. Surface potential for the same system as in Fig. 1. Solid line is for the strongly adsorbed component and dotted line for the weakly adsorbed component.

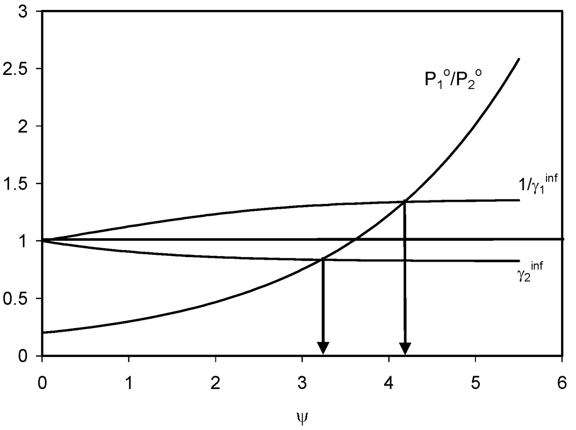


Figure 3. Range of conditions (delimited by the arrows) where azeotropes are observed in the multisite Langmuir model.

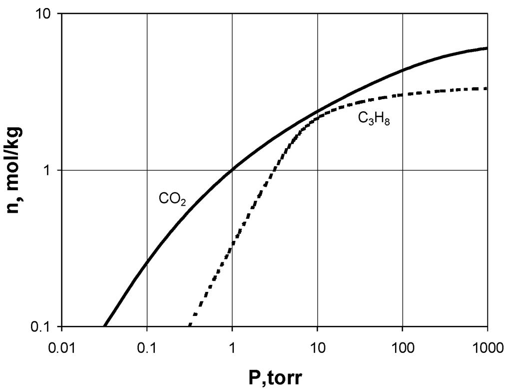


Figure 4. Single component adsorption isotherms for CO_2 (solid line), and C_3H_8 (dotted line) on NaX (Siperstein and Myers, 2001).

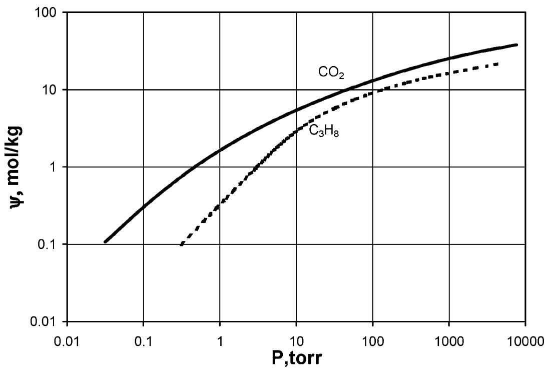


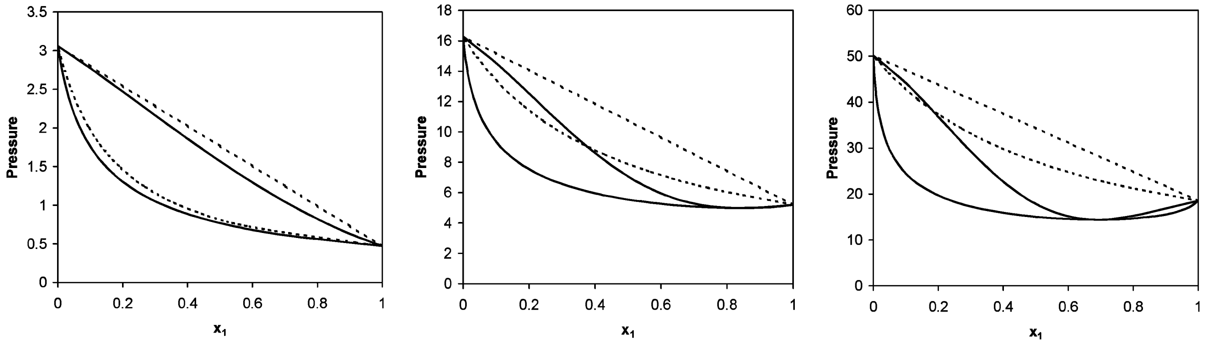
Figure 5. Surface potential for the same system as in Fig. 4.

deviations from ideal solution). The range of conditions where azeotropes can be observed is for values of ψ between 3.2 and 4.2 mol/kg (see Fig. 3). For higher values of ψ, a complete reversal in selectivity is observed.

Also interesting is the case where isotherms do not cross, but the mixtures show azeotropic behavior, as for CO_2-C_3H_8 on NaX (Siperstein and Myers, 2001). The pure component isotherms and the surface potential as a function of pressure are shown in the Figs. 4 and 5 respectively. Figure 4 shows that at approximately $P = 10$ torr the isotherms approach each other. As opposed to the multisite Langmuir model, in this case, for pure components, the amount adsorbed of the small molecule (CO_2) is always higher than for the large molecule (C_3H_8). The favorable adsorption of CO_2in NaX is due to the quadrupole-ion interactions.

Mixture properties have been correlated for this system, and using the ABC equation (Siperstein and Myers, 2001), it is possible to calculate phase diagrams at constant surface potential, as the ones shown in Figure 6. At low surface potentials, the system behaves close to ideal, and as the surface potential increases, strong deviations are observed, including the formation of azeotropes at high CO_2 concentrations. As the surface potential is increase, the azeotrope moves towards lower CO_2 concentrations, nevertheless, this does not suggests a reversal in selectivity because to observe that, it would be necessary to invert the pure component pressures. It is not clear whether the azeotrope would remain at higher pressures, but it was not possible to determine it, as it would have required large extrapolations from the available experimental data.

Figure 7 shows the curves for γ_2^∞ and the ratio p_1^o/p_2^o as a function of pressure for the CO_2-C_3H_8 on NaX. Azeotropes are formed at surface potentials slightly lower than 2 mol/kg and their presence remains over a wide range of densities. In this case, the strong nonideal behavior comes from the interactions between the CO_2 quadrupole moment and the



(a) (b) (c)

Figure 6. VAE curves at constant temperature and surface potential for CO_2-C_3H_8 on NaX calculated with the ABC equation (solid line) and with IAS (dotted line). (a) $\psi = 1$ mol/kg, (b) $\psi = 4$ mol/kg, and (c) $\psi = 6$ mol/kg.

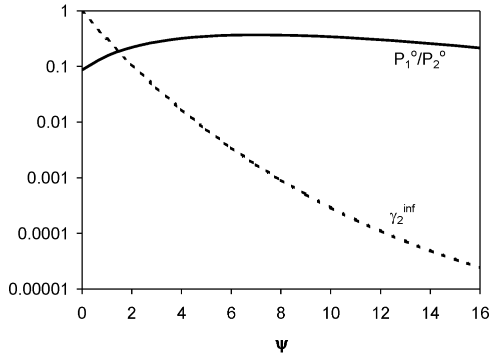


Figure 7. Range of conditions for azeotrope formation in carbon dioxide-ethane mixtures on NaX.

non-framework cations of the zeolite, whereas C_3H_8 is nonpolar. This case is similar to those observed for acid gases and propane on H-mordenite (Talu and Zwiebel, 1986).

4. Conclusions

In this work, it is shown that when pure component isotherms cross at one point, there is a relatively small window of conditions where azeotropes are formed, and reversal in selectivity is observed at high pressures. It is also shown that crossing of pure component isotherms is not necessary to observe azeotropic behavior. Strong nonidealities induced by energetic heterogeneity can result in values of activity coefficients that will give azeotropic behavior, regardless whether the pure component isotherms cross or not.

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