Comments

Comments on "Pure and Multicomponent Adsorption Equilibrium of Carbon Dioxide, Ethylene and Propane on ZSM-5 Zeolites with Different Si/Al Ratios" (Calleja, G.; Pau, J.; Callas, J. A. *J. Chem. Eng. Data* 1998, *43*, 944−1003)

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Recently, Calleja, Pau, and Calles (1998) reported on the adsorption equilibria of carbon dioxide, ethylene, and propane and their binary and ternary mixtures on ZSM-5 zeolites with three different silicon-to-aluminum ratios: 15, 29, and 60 at temperatures of 281, 293, and 308 K. They stated that these experiments are important from the viewpoint of industrial applications and from the interest to gain more knowledge on the insights of adsorption behavior. Moreover, such an excellent experimental study is—from our viewpoint—essential for improving the predictive tools available to precalculate adsorption equilibria.

The conclusion that the Si/Al ratio of zeolitic frameworks modify the behavior in pure and mixture adsorption is not entirely new. But it is not mentioned here anywhere. Since 1976 it has been well-known, as demonstrated by Chen (1976), who described the adsorption of cyclohexane and water onto progessively dealuminated mordenite. Weitkamp (Berke et al., 1991), for example, uses the hydrophobicity index to classify dealuminated zeolites with respect to their adsorption behavior. Also in our group, systematic investigations on the adsorption behavior of a polar and a nonpolar adsorptive on Y zeolites with different Si/Al ratios were undertaken (Sakuth et al., 1995). Here, it was found that the information on ideal and nonideal mixture adsorption is already included in the pure adsorption isotherms. In the Calleja et al. (1998) paper such effects were not studied at all. Even by using the IAST model (Myers and Prausnitz, 1965) adsorption azeotropic behavior can be indicated by predicting an equilibrium curve near the diagonal line in a $y-x$ diagram, i.e., a selectivity value near 1.

The text leads to a misunderstanding (see page 996, section 3.1), that the selectivity in the mixture adsorption can be interpreted by the pure adsorption capacities of the molecules on the three different adsorbents. Calculating the saturation loading of ethylene and propane on the ZSM-5 samples with Si/Al ratios of 15 and 60 by the pure isotherm model of O'Brien and Myers (1984) (see Table 1), the decrease of n_{mi} is nearly the same. However, this decrease cannot only be explained by polarity. Perhaps, it can also be caused by a reduction of the unit cell volume of ZSM-5 through a decrease in the aluminum content. [In general, the trivalent aluminum ion is larger than the tetravalent silicon ion. Therefore the unit cell volume of zeolitic structures contracts with increasing Si/Al ratio (Szostak, 1989). In the case of ZSM-5 this dependency is much more complicated due to phase changes. As Kokotailo et al. (Kokotailo, Riekert and Tissler, 1989) demonstrated, these phase changes are strongly linked to the type of adsorptive and the number of adsorbed molecules per unit cell.] The "polarity effect" can even better be observed by the slope of the pure adsorption isotherms at low adsorptive pressures, i.e., the differences in the energetical factor b_i and the standard deviation of the energetical distribution of adsorption sites called ρ_i.

Using the pure isotherm parameter of Table 1 and the PRAST model (Sakuth et al., 1998) for an adsorption mixture prediction, it can be shown (see Figure 1a,b) that

Table 1. Fitted Isotherm Parameters (T = 293 K)[a]

isotherm equation of O'Brien and Myers	n_{mi}, mmol/g	b_i, kPa^{-1}	ρ_i
ethylene on ZSM-5 with a Si/Al ratio of 15	1.9787	0.8685	2.2523
ethylene on ZSM-5 with a Si/Al ratio of 60	1.5664	0.1157	1.2885
propane on ZSM-5 with a Si/Al ratio of 15	1.6742	3.1114	2.2503
propane on ZSM-5 with a Si/Al ratio of 60	1.3310	2.1292	1.5062

[a] n_{mi} = saturation loading; b_i = energetical factor.

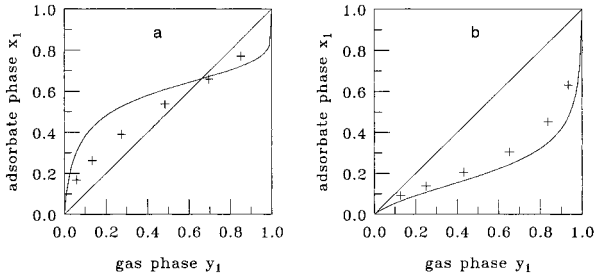

Figure 1. Binary adsorption equilibrium of ethylene (component 1, +) and propane (component 2) on ZSM-5 zeolite with Si/Al ratios of 15 (a) and 60 (b) at approximately 80 kPa and 293 K. The line represents the prediction results using PRAST at 6 kPa. (Hence, in the experiments a nearly pressure independent mixture behavior is found: it follows that a simplified prediction at 6 kPa is possible here.)

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the azeotropic mixture behavior on ZSM-5 with a Si/Al value of 15 and the nearly ideal mixture behavior on ZSM-5 with a Si/Al value of 60 are consistent with the pure isotherm data.

In the paper, it also has to be clarified how to calculate the saturation pressure P^S of ethylene at 293 and 301 K, which is needed in eq 2 (see page 997) for the estimation of the free energy of immersion. At these adsorption temperatures ethylene is usually above its critical temperature, which is 282 K.

Calleja et al. (1998) found in their studies that mixtures of molecules with similar polarities (ethylene and CO_2) show an ideal adsorption behavior at low Si/Al values (medium-pore ZSM-5 with Si/Al ratio of 15), which is independent from adsorption pressure. This observation is remarkable and has to be discussed in detail, because real adsorption behavior of an ethylene−CO_2 mixture (P = 6 kPa) on small-pore zeolite 5A (Si/Al ratio of 1) is reported by Persichini and Mersmann (1990), whereas a nearly ideal behavior of these molecule mixtures is described by Hyun and Danner (1982) on wide-pore zeolite 13X at nearly the same low Si/Al ratio (Si/Al ratio of 1.25; P = 138 kPa).

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