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Reply to Comments by M. Sakuth, S. Sander, and J. Gmehling on *J. Chem. Eng. Data* 1998, *43,* 994−1003

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Sakuth, Sander, and Gmehling (preceding paper in this issue) have made some comments on the above-mentioned article published by Calleja, Pau, and Calles (1998). They basically say that the results obtained by Calleja et al. do not mention other previous publications where the behavior of mixture adsorption is modified by the Si/Al ratio of zeolitic frameworks and that there is a misunderstanding (page 996, section 3.1), that the selectivity in the mixture adsorption could be interpreted by the pure adsorption capacities of the molecules on the different adsorbents. They also argue that the information on ideal and nonideal mixture adsorption is already stored in the pure adsorption isotherms, according to their studies (Sakuth et al., 1995), and that even by using the IAS model adsorption azeotropic behavior is indicated by predicting an equilibrium curve near the diagonal line in a $y-x$ diagram.

It seems that Gmehling et al. have not realized a significant difference between the zeolites used in our work and those used by them and by other authors mentioned by them regarding the Si/Al ratios.

All the samples of Y zeolite used by Gmehling et al. have been obtained by progressive dealumination techniques using the $SiCl_4$ method of Beyer and Belenykaja (1984), whereas each of three ZSM-5 zeolites used by Calleja et al. (Si/Al ratios: 15, 29, 60) have been obtained by direct synthesis, changing the reaction conditions, according to a well-established procedure (Costa et al., 1987) where no dealumination takes place.

This is a significant difference, because in the dealumination process there is not only a decrease in the aluminum content of the zeolite but also a significant modification of the microporous structure of the zeolite. Even part of the remaining Al can be extraframework, giving a different product with different properties with respect to the original zeolite. This has been clearly stated by Kawai and Tsutsumi (1998), who have found that $SiCl_4$ treated samples of Y zeolites—similar to those used by Gmehling et al.—showed lower adsorption capacities, attributable to partial destruction of the zeolite framework, with secondary pure structure appearance.

It is obvious that this is not the case of the ZSM- 5 zeolites used in our work, since the differences in Si/Al ratios were the result of different synthesis conditions and not of any dealumination process. Moreover, the structural changes of the zeolites during the dealumination process are stronger for aluminum rich zeolites, like the Y zeolite, so that even for a dealuminized ZSM-5 zeolite (which is not the case in our work) the differences would still be significant.

Consequently, no mention of other previous works with dealuminized zeolitics was included in our paper, because the comparison would produce a misunderstanding and possible confusion.

On the other hand, in the publication of Calleja et al. (1998), it is not said that the selectivity in the mixture adsorption could be interpreted by the pure adsorption capacities of the molecules on the different adsorbents (page 996, section 3.1). This is a misunderstanding of the readers, since what is said is that the experimental results can be explained in terms of the differences in molecular structures of the various adsorbates, that is, in terms of their different polarities, which determine different interactions with the electrical field inside the micropores of the zeolites. It is clear that electrostatic effects give rise to significant differences in the adsorption mixture behavior, as noted by different authors (Dunne et al., 1996; Calleja et al., 1994; Costa et al., 1991), and this is the basis for the explanation of the results of mixture adsorption on ZSM-5 zeolites, as commented in the paper. There is no reduction of the unit cell dimension, as suggested by Gmehling et al. (previous paper in this issue), simply because there is no dealumination at all.

Although the decrease in the saturation loading of ethylene and propane with Si/Al ratio of ZSM-5 zeolites calculated by the pure isotherm model of Myers and O'Brien is similar, as shown by Gmehling et al. in Table 1 of the previous paper in this issue, it is clear and explicit from experimental results of Figure 1 of the paper by Calleja et al. that the effect of the Si/Al ratio is much stronger on the ethylene isotherm than in the propane isotherm and even stronger on the CO_2 isotherm. It is evident from this figure—which corresponds to experimental data, not to any model fitting—that the polar molecules such as ethylene and CO_2, as compared to the nonpolar molecule of propane, are much more strongly influenced by the Si/Al ratio of ZSM-5 zeolite, showing a considerable decrease in adsorption loading in the range 0−100 kPa with increasing Si/Al ratios. In others words, ZSM-5 zeolites with low aluminum content (Si/Al = 60) adsorb preferentially propane, and ZSM-5 zeolites with relatively high aluminum content (Si/Al = 15) adsorb preferentially CO_2 and ethylene, which are polar molecules with a significant quadruple moment.

Concerning model prediction, we are sorry that the comparison of mixture experimental data and model prediction with IAS and RAS models, also done in our work, was not included in the publication due to editorial limitations (this part will be published elsewhere), since the main purpose of the Journal is to publish data rather than model predictions. Anyway, there are some significant comments to make, as shown below.

It is not acceptable to say that the information on ideal/nonideal mixture behavior is already stored in the pure adsorption isotherms and that the IAS model can indicate an azeotropic behavior by predicting an equilibrium curve near the diagonal line in a $y-x$ diagram, as said by Gmehling et al. We just fully disagree with this statement,

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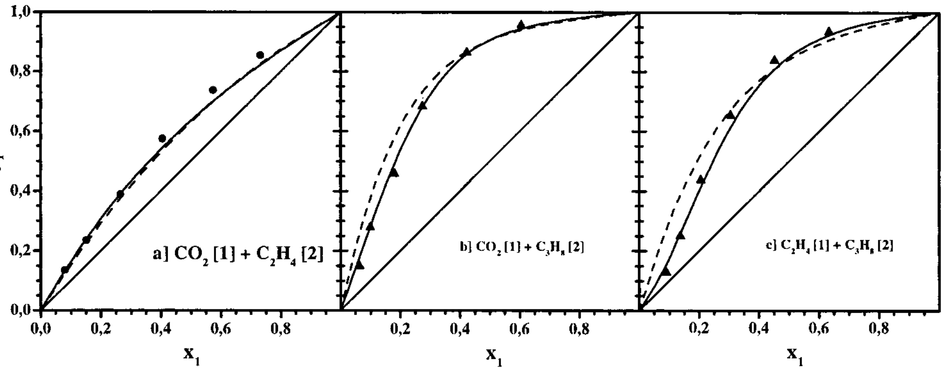

Figure 1. Experimental and prediction binary adsorption equilibrium on ZSM-5 zeolite (Si/Al = 60) at 80 kPa and 293 K: circles, experimental; dashed line, IAS model; solid line, RAS model.

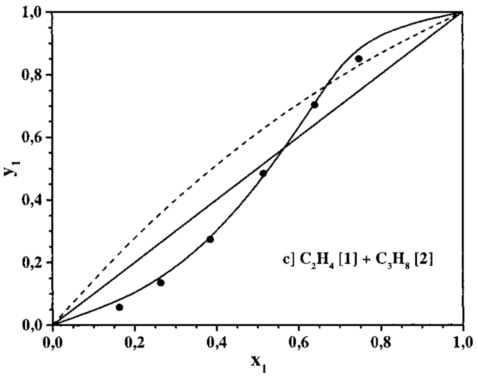

Figure 2. Experimental and prediction binary adsorption equilibrium on ZSM-5 zeolite (Si/Al = 15) at 80 kPa and 293 K: circles, experimental; dash line, IAS model; solid line, RAS model.

which is really a misunderstanding. The IAS model cannot predict any nonideal behavior in mixture adsorption. And nonideal behaviors include not only the azeotropic behavior but also any deviation from the ideal $y-x$ curve that is symmetric with respect to the second diagonal line of the $y-x$ diagram. Therefore, it is not acceptable that the IAS model predicts a system which shows an adsorption azeotrope just because the model at least predicts an equilibrium curve “near” the diagonal line.

So, for systems with no azeotrope, IAS model predictions where the symmetric $y-x$ theoretical curve does not fit with the experimental data cannot be considered as good predictions, and consequently a nearly ideal behavior cannot be stated. However, Gmehling et al. seem not to agree with this (Sakuth et at., 1995, page 898 and Figures 4 and 5 for DAY-100). In the data reported by Calleja et al. (1998), the ethylene−propane mixture on ZMS-5 (Si/Al = 60) cannot be considered as ideal, although it does not show any azeotrope. Only the CO_2−ethylene mixtures show ideal behavior, as shown by Figure 5 of Calleja et al. (1998).

These can be clearly illustrated by Figures 1 and 2 of these comments, where IAS and RAS model predictions have been compared to the experimental data, as will be shown in a future publication. As observed, the RAS model curves show a better data fitting compared to those shown by Gmehling et al. in their comments (Figure 1a,b). Anyway, we agree that these data are consistent with the pure isotherm data and that an increase in the Si/Al ratio of the zeolites produces a closer behavior to ideality.

We also agree that the ideal adsorption behavior of the CO_2−ethylene system can be remarkable, but it is consistent with other data (Hyun and Danner, 1982; Calleja et al., 1994) where the same ideal behavior is observed with 13X zeolite. However, the behavior of this mixture on 5A zeolite (Persichini and Mersmann, 1990) is nonideal, which is probably related to the very low value of the Si/Al ratio in this zeolite (Si/Al = 1) compared to the ZSM-5 zeolite (Si/Al = 15). This difference can be important concerning the ideal/nonideal behavior.

In summary, we agree with Gmehling et al. that the Si/Al ratio influences the ideal/nonideal behavior of a given mixture. The differences are in the interpretation and also in the limitations coming from the differences between dealuminized zeolites and low aluminum zeolites by direct synthesis. Gmehling et al. base their explanations of nonideallities on surface heterogeneity, that is, surface hydrophobicity, whereas Calleja et al. base their interpretations on the different molecular interactions with the zeolite surface which depend on the polarity of the molecules. Probably both approaches are acceptable and represent part of the same reality.

A last consideration about the calculation of the saturation pressure of ethylene at 293 and 301 K is needed for eq 2 (page 997): It is true that it is not possible to calculate saturation pressures above the critical conditions. In this case, if the temperature is not much higher than the critical temperature, most researches accept the extrapolation from the critical value according to the Riedel equation:

$$\ln P_s = A + \frac{B}{T} + CT + DT^3$$

In our work we have also used this equation to calculate P_s for ethylene at $T > T_{crit}$.

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