Reply:

We are thankful to Krishna and Van Baten for the careful attention given to our article "Diffusion Under Pore Saturaton Conditions", and for their challenging comments and criticisms. We acknowledge their huge and enlightening contributions to the modeling and analysis of multicomponent diffusion, including the recent references mentioned in their Letter to the Editor and not quoted in our article.

Nevertheless, we must disagree with the arguments they develop in their Letter to the Editor to oppose our model, and also with certain interpretations based on their own modeling approach.

Our reply is organized along two points, which are later further developed.

Letting the cross-coefficients $1/Ð_{ij}$ in the Maxwell-Stefan matrix go to zero *is not* a fundamental constitutive assumption of our model. Even in the absence of cross-coefficients $1/Ð_{ij}$, strong couplings may arise from the thermodynamic and steric effects.

Our experimental results under saturation conditions cannot be properly interpreted by Krishna and Van Baten's model, even in the most recent version mentioned in their Letter.

Point 1

In their letter to the editor, Krishna and van Baten insist on the importance of taking into account the exchange coefficients when dealing with mixture diffusion under conditions of pore saturation, and express the conviction that in not doing so, we build a model that is "fraught with danger" and that cannot explain certain observed phenomena.

For the purpose of this discussion, we may best start from a statement near the end of their letter that directly hits the fundamental aspects: "The approach taken by Lettat et al. in developing their diffusion model for pore saturation conditions is fundamentally different to the one we have adopted. A key assumption they make is $Ð_{ij} \Rightarrow \infty$". We do agree with the first sentence of this statement, but disagree with the second.

The fundamental difference is not that considered by Krishna and Van Baten. The assumption $1/Ð_{ij} \Rightarrow 0$ is in no way necessary to the development of the model (as a matter of fact, we first developed it with a full Maxwell-Stefan diffusion matrix, without any additional mathematical difficulty). This simplification was made in our article only to adapt the model to the system at hand, that is, C6 isomers in MFI zeolites, where we think it is justified. However, of course, the presence or not of these cross-coefficients affects the use of the model for interpreting experimental results.

In our view, the fundamental difference lies in the way the complexity of the "correlations" or "couplings" is accounted for:

– In Krishna and Van Baten's approach, the "correlations" or "couplings" are exclusively accounted for, and interpreted by, the cross-coefficients $Ð_{ij}$.
– In our approach, two additional effects are introduced at the microscopic level, the thermodynamic equilibrium, and the steric constraints (through the molar volume effects).

The rational and consistent combination of these effects with Maxwell-Stefan's equations, at the microscopic level, in the framework of a dusty-gas formulation, and with the use of volumic concentrations, constitute the fundamental originality of our model.

The "microscopic level" here means that of the nanopore space inside the zeolite crystals; thermodynamic equilibrium is not just a boundary condition at the crystal surface or at some other macroscopic level, as is done in many modeling approaches. In other words, the two additional effects are fully integrated in the description of the diffusive process itself. It is also worth highlighting the implications of the dusty-gas approach: it introduces a N + 1th species allowing independence of the diffusion coefficients without recourse to the notion of vacancies, used in Krishna and Van Baten's approach. The point is that at full saturation, vacancies have completely disappeared, a degree of freedom is lost, and the diffusion coefficients are subject to an additional constraint in their model (they are no longer independent). This inconvenience does not occur in our model.

We do not dispute the pertinence of M-S models containing finite $Ð_{ij}$ cross-coefficients for certain situations, for example, in the case of self-diffusion in an unary system as discussed in Krishna and Van Baten's letter, where thermodynamic and steric effects would play no role. As a matter of fact, we do note in our article that "the Maxwell-Stefan binary exchange diffusion coefficients $Ðij$ — which represent the interactions between components i and j — might not be negligible anymore". However, what we claim is that in the case at hand and similar ones (i.e., mixtures of isomers of molecular dimensions close to pore size, and saturation), even in the absence of cross-coefficients $Ð_{ij}$, strong coupling may be due to the thermodynamic and steric effects.

Point 2

Krishna and Van Baten write: (For the correlation-dominant case and equimolar mixtures) "All the elements of the matrix are equal to one another, and there is just one characteristic diffusivity. This is an intuitively rational result; when correlations are dominant, the differences in the diffusivities get washed out".

This implies that at saturation, there is no longer any diffusional selectivity. On the contrary, our results indicate that strong diffusional selectivity may still exist at saturation. For example, in our breakthrough experiments, 3-methylpentane and 2-methylpentane have time enough to diffuse into the zeolite framework and reach quasi-equilibrium, whereas 22DMB hardly penetrates the solid structure. This behavior is logically reflected in our model by the single-component diffusivities of the species (the diagonal coefficients $Ð_{ii}$), which differ by orders of magnitude, but cannot be represented if there is "just one characteristic diffusivity". In a forthcoming article, this behavior will be studied in more detail and confirmed by cyclic experiments on this system.

Conclusion

We do agree that neglecting the cross-coefficients is a simplification and might reduce the precision of our model or its ability to predict some special or some more complex diffusion behaviors. Incorporating the cross-coefficients into our model introduces no mathematical complexity, just additional parameters.

We also agree that the full Maxwell-Stefan approach developed and used by Krishna and Van Baten is coherent, sufficient, self-standing and useful in most (if not all) situations far enough from saturation.

On the other hand, we claim that the simplification of cancelling the $1/Ð_{ij}$ is justified in our type of system, and highlights the fact that nonlinear coupling (correlation) may be due to other essential phenomena, thermodynamic equilibria and steric effects, the latter effects may be incorporated rationally and rigorously into the microscopic formulation of the diffusion model, as an alternative to a "pure" Maxwell-Stefan formulation at full saturation, there may still exist a strong diffusional selectivity, reflected in our model, but contrary to the prediction of the full Maxwell-Stefan model as presented by Krishna and Van Baten in their Letter to the Editor, their interpretation of cross-effects exclusively through the role of the cross-coefficients $Ð_{ij}$ is "fraught with danger" at saturation, due to extrapolating the vacancy approach, ignoring the volume constraints resulting from different molar volumes of the species, and neglecting the effects of the interactions of the species with the solid matrix.

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