

# Configurational Entropy and Intersection Blocking Effects in Multi-component Systems in MFI-type Zeolites Studied by IR Microscopy

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## 1. Introduction

Diffusion is important in many technological processes, particularly those that utilize nanoporous materials like zeolites for adsorptive separations and catalysis, where mass transfer is often the rate-limiting step. For understanding and predicting such processes knowledge of the adsorption and diffusion behaviour of molecular mixtures is essential.

It is known, that branched hydrocarbons like 2-methylpentane favor the intersections of the channels in MFI-type zeolites as adsorption sites and therefore may impede separation processes by “intersection blocking” [1-3]. On the other hand, in molecular simulations “configurational entropy effects” are found predicting that at higher loadings the sorption of linear alkanes is favored above branched alkanes, if molecules with the same C-number are compared. In this study we present a direct experimental evidence of the “configurational entropy effect” in MFI-type zeolites and cross-link the results with the occurrence of “intersection blocking”.

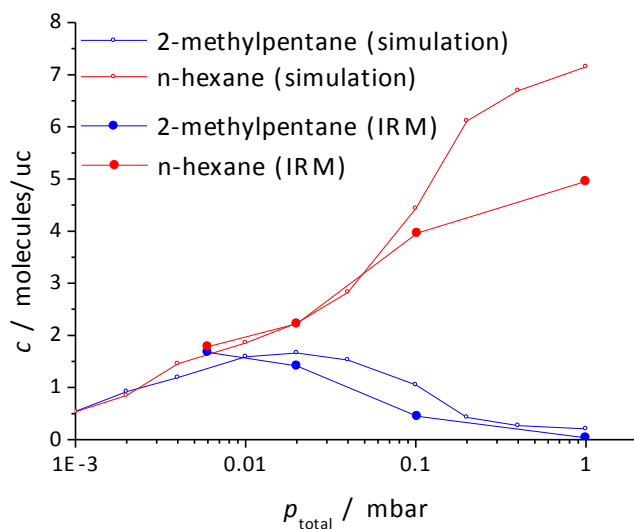
## 2. Experiment and Results

IR Microscopy (IRM) is a suitable technique to investigate molecular mixtures, since it is possible to observe different components simultaneously by their characteristic IR bands. In our experiment we chose a MFI type zeolite (silicalite-1), which is one of the most important frameworks in separation processes. As adsorbate we applied a 1:1 mixture of 2-methylpentane and (fully deuterated) n-hexane, in order to investigate the entropy effects predicted in simulations [1]. n-Hexane was used in the fully deuterated form to easily distinguish the two components in the IR spectra.

Figure 1 displays the measured mixture isotherms in comparison to the results of CBMC simulations published in [1]. Both, experiments and simulations are in good agreement with each other. For total loadings below 4 molecules/uc the adsorbed amounts of both molecules are roughly equal. However, as predicted by the CBMC simulations, above 4 molecules/uc the effect of “configurational entropy” comes into play. 2-Methylpentane is then pushed out gradually due to the fact that the n-hexane molecules can be packed more efficiently into the channels of the MFI-type structure.

“Intersection blocking” describes the slowing down of fast diffusing molecules (e.g. linear alkanes) if tardy molecules (e.g. branched alkanes) occupy the intersections of the channels in the MFI-type structure. In agreement with predictions of simulations [1] and our previous study [2] we found that the n-hexane mobility is reduced by “intersection blocking” only if the partial loading of 2-methylpentane approaches or exceeds 2 molecules/uc [4]. In turn we can conclude that “intersection blocking” is insignificant for an n-hexane/2-methylpentane separation by MFI-type structures, at least at high

pressures. This is in contrast to the n-butane/isobutane system where the effect of “configurational entropy” is less pronounced and, hence, mixture diffusion is strongly dominated by “intersection blocking” at high pressures which e.g. excludes the use of MFI-membranes for a separation of these C4 alkanes [2,3].



**Figure 1:** Isotherms of a 1:1 gas phase mixture of n-hexane and 2-methylpentane at 298 K measured with IRM and compared to CMBC simulation data (replotted from [1]). The decreasing loading of 2-methylpentane for  $c_{\text{total}} > 4$  molecules/uc is a direct experimental evidence of the “configurational entropy effect”.

## References

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