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Influence of Phase Transitions on the Mobility of Organic Pollutants in Synthetic and Natural Polymers

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1. Introduction

Transport and availability of organic pollutants in soils, sediments and aquifers are closely related to the interactions of these compounds with the natural organic polymers (so-called soil organic matter [SOM], e.g. humic substances) present in these media. Contaminants may be either immobilized and retarded (and sometimes conserved for decades [1]) or transported by dissolved organic matter. The mechanistic insight and the quantitative description of these (often not completely understood) processes have a crucial significance for the fate of these chemicals in the environment and for remediation tasks.

It is well known from amorphous synthetic polymers that they can exist in two states: a glassy one with a more rigid structure and a rubbery one with higher flexibility. The phase transition can have a marked influence on the mobility of guest molecules in these materials. Some recent and partly controversially discussed results provide indications for such a phase transition also occurring in humic substances and native SOM [2,3]. The phase transformation may be initiated by temperature and/or humidity changes.

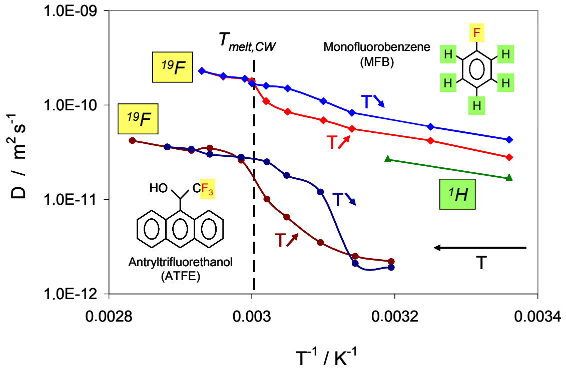
Because conventional thermo-analytical methods alone are not suitable for clarifying this hypothesis, a combination of microscopic (diffusion measurements by pulsed field gradient [PFG] NMR) and macroscopic techniques (temperature-programmed desorption [TPD]) has been applied in this investigation to detect the structural changes by their influence on the mobility of probe molecules. To eliminate the natural background in the case of NMR experiments, fluorinated organic compounds were used. Especially PFG NMR provides the ideal possibility to evaluate the migration of the probes as an indicator for the phase constitution without disturbing the complex system.

2. Experimental

As synthetic organic matrices, substances exhibiting no (a commercial compound with a phenyl ether structure [Tenax®]), first-order (n-eicosane and poly[ethylene glycol] with the commercial name Carbowax [CW]) and second-order phase transition (polystyrene) in the temperature range investigated, were studied. As natural polymers, humic acids (from Roth and Aldrich) were applied. Additionally, thermodesorption experiments were carried out with originally contaminated soil samples having an SOM content of less than 1 wt.-%. However, this content is known to be sufficient to bind hydrophobic pollutants present in the soil sample.

The probe molecules for the thermodesorption experiments and the diffusivity measurements were mono- and hexafluorobenzene, octafluoronaphthalene and 9-anthryltrifluoroethanol. Additionally, toluene was used for the thermodesorption from a humic substance. In the real-contaminated samples a wide spectrum of hydrocarbons (BTEX and polycyclic aromatics, partially substituted) was found.

3. Results and discussion



Diffusion coefficient of fluorinated probe molecules in CW as determined by ^{19}F and ^{1}H PFG NMR spectroscopy

As shown in the figure, a first-order phase transition could be clearly detected by PFG NMR due to its influence on the mobility of fluorinated compounds in the synthetic polymer CW. Similar results were obtained by thermodesorption experiments. In contrast, no discontinuous behaviour was found in the case of Tenax having no phase transition in the temperature range evaluated.

In the TPD experiments, the first- and second-order phase transitions led to a significant increase in the release of certain organic probe molecules into the gas phase thus giving a second peak in the thermodesorption runs. However, the distinctness of this two-phase behaviour significantly depended on the substance and its initial concentration.

For pure humic substances and real-contaminated samples, the influence of water on the mobility of organic probe molecules and organic pollutants could be demonstrated. This result can be interpreted by the action of water as “emollient” of the SOM thus initiating a phase transition. The PFG NMR studies with natural polymers are in progress.

4. Conclusions

The evaluation of the mobility of probe molecules by PFG NMR spectroscopy (on a microscopic scale) and their thermodesorption (macroscopic scale) has been shown to be a suitable method to detect phase transitions in synthetic and natural polymers. The application of these techniques to humic substances and contaminated soils will be continued.

References

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