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Sorption of volatile organic compounds and their mixtures on montmorillonite at different humidity



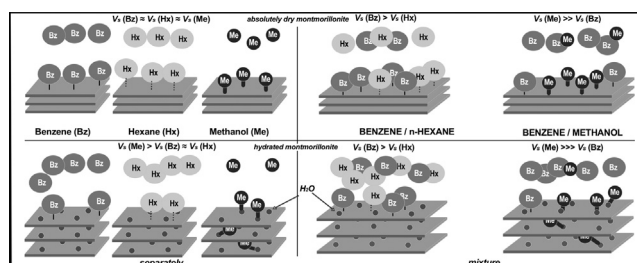
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HIGHLIGHTS

- Absolutely dry mineral was non-selective towards benzene, n-hexane and methanol.
- Hydration inhibited sorption of hydrocarbons and promoted that of methanol.
- Binary mixtures even hydrocarbon mixture equal by volume were sorbed competitively.
- Benzene in the mixture was more active than n-hexane at all humidity levels.
- Methanol was dominantly sorbed from benzene/methanol mixtures at all volume ratios.

GRAPHICAL ABSTRACT



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ABSTRACT

The vapor-phase sorption of volatile organic compounds (VOCs), i.e. n-hexane, benzene and methanol, along with sorption of their binary mixtures, i.e. benzene/n-hexane and benzene-methanol, on montmorillonite with different water content was studied. The absolutely dry mineral did not exhibit selectivity towards the studied VOCs sorbed separately. The hydration inhibited sorption of hydrocarbons and promoted that of methanol because of intercalation of its molecules to the interlayer space of the swelling mineral and dissolution in the water films on the external mineral surface. Unlike separate sorption of benzene and n-hexane, sorption of their binary mixture on the montmorillonite, even equal by volume, was selective. The components shared the same sorption sites with benzene being more active due to its ability to form the donor-acceptor complexes with the mineral surface in addition to Van-der-Waals interactions. Opposite, in the benzene/methanol mixture the undoubted predominance of hydrophilic methanol over benzene was revealed, which increased with increasing humidity and was significantly stronger compared to the differences in sorption of methanol and benzene sorbed separately. In the binary mixtures unequal by volume, preadsorption played an important role in VOCs competition with sorption of aliphatic n-hexane being suppressed stronger than that of aromatic benzene. In the benzene/methanol mixture, methanol was predominantly sorbed at all the studied volume ratios and hydration degrees, occupying its specific sorption sites. Hydration of the montmorillonite caused the reverse impact on the sorption of benzene and methanol. As a result, at the full hydration state methanol sorption in the mixture reached that of the pure methanol.

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1. Introduction

Volatile organic compounds (VOCs) are hazardous pollutants. Their usage as solvents in chemical and light industry together with volatility of light oil fractions transported around the world leads to widespread environmental pollution [1–3]. Most of them are carcinogenic and directly affect human health. Moreover, their ability to accumulation results in long-term indirect influence on health. Among various methods, sorption is considered the most effective and easy implemented method of VOCs elimination from air, water and soil environments [4–8]. Existing sorption methods of VOCs removal mainly utilize expensive synthetic sorbents, such as synthetic activated carbons and zeolites [9,10]. Despite high effectiveness of these sorbents, they have a number of significant drawbacks such as expensive synthesis, difficult regeneration and, in case of activated carbons, low mechanical stability. Therefore, research aimed at alternative sorbents such as clay minerals and mechanisms of their sorption activity are highly relevant.

Unlike activated carbons and zeolites, clay minerals are physically and chemically stable, easily regenerated and widely broadcasted: estimated deposits of Ca-bentonite alone consist of 2.5 billion tons of material [11]. Analysis of recent literature data shows the relevance of the study of their sorption activity. Clay minerals were found effective in removal of dangerous organic contaminants such as organic compounds of various classes (acetone, benzene, toluene, *o*-xylene [12–14]), antibiotics widely used in agriculture [15–17], common textile industry dyes [18–20], etc. Besides, revealing the mechanisms governing VOCs sorption on clay minerals as the major soil component, is extremely important for the development of soil remediation technologies. Cheng et al. [21] in their review imply that understanding the mechanisms of sorption of organic contaminants on soil minerals is important for both fundamental and practical research. He emphasizes that sorption in mineral micropores (<2 nm) plays a key role in controlling their fate and transport when the porous geological media have very low organic carbon contents (<0.1%).

In real gaseous and liquid systems VOCs are presented mainly in mixtures and therefore, they compete for sorption sites with minimal free adsorption energy. For optimizing processes of remediation and separation of such mixtures, knowing the mechanisms of not only sorbate–sorbent but also sorbate–sorbate interactions is crucial. The presence of moisture in the mixture increases the competition in the sorption system. This information is generally gathered from isotherms of sorption of VOCs mixtures. However, research is concentrated mainly on the liquid-phase sorption of VOCs [22–26], whereas investigation of their competitive vapor-phase sorption is scarce because of experimental difficulties. Still, in the vapor phase the information on mechanisms of sorbate–sorbate interactions is the most precise to describe their competition in a mixture in both dry and wet (when water competition takes place) conditions.

Montmorillonite has been actively studied as a promising sorbent for the purification of gas/air mixtures [27–30]. Cheng and Cheng [31] studied sorption of a HP Petrochemical Standards mixture containing (by volume) 69% methane, 9% ethane, 6% propane, 3% *n*-butane, 3% *i*-butane, 1% *n*-pentane, 1% *i*-pentane, 0.5% *n*-hexane, 6% nitrogen, 1% carbon dioxide, and 0.5% oxygen, on kaolinite, Na-montmorillonite, humic coal and oil shale. As compared with sorption on the activated carbon, the adsorption on clay minerals was less but still significant. The adsorption selectivity among the C₂–C₆ hydrocarbon gases has also been quantified and it has been confirmed that the selectivity results mainly from the variations in their vapor pressures.

It is known that competition with water can significantly reduce sorption of hydrophobic organic contaminants in mineral micropores by making the hydrophilic pore spaces inaccessible for organic

Table 1

Physical–chemical characteristics of the K-10 montmorillonite sample.

Unit cell	(Na,K)(Al,Mg) ₆ (Si ₄ O ₁₀) ₃ (OH) ₆ · <i>n</i> H ₂ O
CEC	90 meq/100 g
Exchangeable cations	Na, K
Specific surface	250 m ² /g
Density	1.8 g/cm ³

molecules, thus in the presence of water hydrophobic organic contaminants primarily adsorb in the hydrophobic micropore spaces of natural and synthetic minerals [32–35]. Lee et al. [36] studied the competitive sorption between trichloroethylene and water vapor on activated carbon and showed that water content affected sorption activity of trichloroethylene after 80% RH. Ong and Lion [37] observed nonlinearity of effect of water content on sorption activity of trichloroethylene on Na-montmorillonite, kaolinite, alumina and iron oxides. In the region from oven-dried solid surface to one monolayer water coverage, strong competition between water and trichloroethylene for adsorption sites on the surface was found. Then trichloroethylene sorption sharply decreased with increasing water content. When water molecules formed more than five layers, its sorption increased gradually because of dissolution in the condensed water phase on the solid interface.

In this study, the vapor-phase sorption of typical VOCs, i.e. aliphatic *n*-hexane, aromatic benzene and aliphatic methanol, along with sorption of their binary mixtures on montmorillonite with different water content was studied. The competition between VOCs sorbed from binary mixtures of hydrophobic/hydrophobic (i.e. benzene/*n*-hexane) and hydrophobic/hydrophilic (i.e. benzene–methanol) compounds at different humidity was identified and quantitatively described.

2. Experimental

2.1. Objects

As sorbent, the K-10 montmorillonite from Aldrich was used; its main characteristics are summarized in Table 1 and XRD patterns are shown in Fig. 1. The montmorillonite samples used in sorption experiments were obtained by purification of commercial

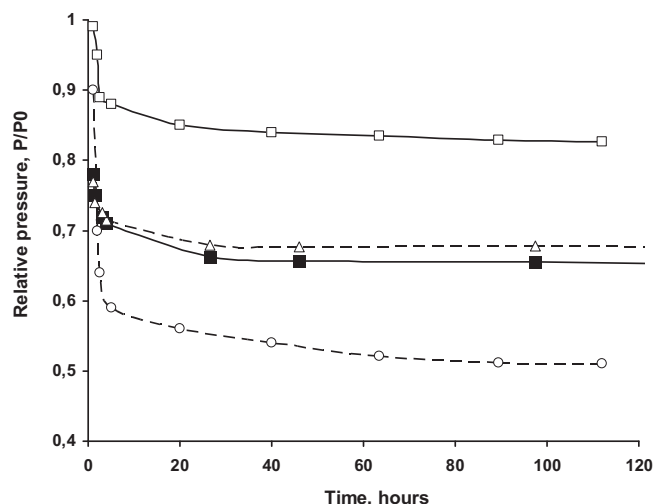


Fig. 1. Kinetic curves of sorption of binary mixtures (1:1 by volume) on the air-dried (5.3 wt.%) K-10 montmorillonite. (■) Benzene in the benzene/*n*-hexane mixture, (△) *n*-Hexane in the benzene/*n*-hexane mixture. (□) Benzene in the benzene/methanol mixture, (○) Methanol in the benzene/methanol mixture.

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