

Effects of solution, sorbate, and sorbent chemistries on polycyclic aromatic hydrocarbon sorption to hydrated mineral surfaces

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<요약문>

Solution chemistry, sorbate chemistry, and sorbent chemistry were widely investigated to find important factors that affect PAH sorption on mineral surfaces and to elucidate its microscopic mechanism. The solution chemistry, pH and ionic strength caused measurable change of HOC sorption reaction to minerals. The detectable change of K_d occurred at a pH region crossing the PZC (Point of Zero Charge) of each mineral. The PAH hydrophobicity, one of sorbate chemistry, was observed to have a strong correlation with PAH sorption to mineral. Mineral surface area was not found to be a predominant factor controlling PAH sorption. The mineral type might be more likely to play a crucial role in controlling the PAH sorption behavior. The CEC (Cation Exchange Capacity) of mineral, representing surface charge density, has meaningful correlation with regression slope of sorption coefficients ($\log K_d$) versus aqueous activity coefficients ($\log \gamma_w$).

key word : Polycyclic aromatic hydrocarbons, Sorption, Mineral, Hydrophobicity, Activity coefficient.

1. INTRODUCTION

Sorption reactions in aqueous environments for polycyclic aromatic hydrocarbons (PAHs) and other hydrophobic organic contaminants (HOCs) are an important process controlling their mobility, chemical reactivity, bioavailability, and toxicity [1]. The distribution of nonionic HOCs between water and surface soils or sediments has been shown to depend primarily on the hydrophobicity of the compound and the fraction of organic carbon (f_{oc}) in the sorbent [2-3]. However, when little organic carbon is present in a sediment or aquifer (e.g., $f_{oc} < 0.001$), values for K_{oc} have been observed to be much higher than would be predicted based on sorption by organic material alone [4]. In these low-organic systems, mineral surfaces are thought to contribute significantly to, and may even control, the sorption of HOCs [5]. Numerous examples of environments that contain low amounts of organic carbon encounter in natural (e.g., ground water aquifers, some sediments, and some atmospheric water drops) and engineered (e.g., landfill liners and slurry walls) environmental systems. Hence, the sorption of HOCs to mineral surfaces

can play an important role in understanding their fate and transport of HOCs in subsurface environments. The objectives of this study were to (1) investigate aqueous chemistry (i.e. pH and ionic strength) effects on PAH sorption to mineral surfaces, (2) elucidate the relationship between aqueous activity coefficients and distribution coefficients on a given mineral for three PAHs, (3) study the influence of mineral surface on PAH sorption to mineral surfaces.

2. MATERIAL AND METHODS

Experiments for PAH sorption to mineral were performed in batch reactor systems. Fifty mL glass centrifuge tubes with Teflon-lined screw caps were used as batch reactors. The minerals were pretreated to remove amorphous iron oxides and organic matter using dithionite-citrate-bicarbonate (DCB) and hydrogen peroxide, respectively. Optimum sorbent concentration was selected within the range of sorbent concentration that yield between 30% and 70% PAH sorption. The suspension was equilibrated for at least four hours, enough to hydrate the mineral surfaces, and the pH and ionic strength were readjusted, if necessary. PAH concentrations in methanol-water mixtures and hexane were measured using fluorescence spectroscopy (PhotonTechnology International, Inc., Brunswick, NJ).

3. RESULTS AND DISCUSSION

Effect of pH and ionic strength on pyrene sorption

Sorption experiments at different pH and ionic strength values for pyrene and minerals were performed to investigate the effect of pH and ionic strength on PAH sorption to mineral surfaces. Fig. 1 (a) depicts the effect of pH on pyrene sorption to mineral surfaces over the wide range of pH. As shown in Fig. 1 (a), pyrene sorption generally increased with decreasing pH when the ionic strength was held constant at 0.1 M NaClO₄. Especially, a noticeable change of K_d values was observed as the pH changed across the PZC (Point of Zero Charge) of each mineral.

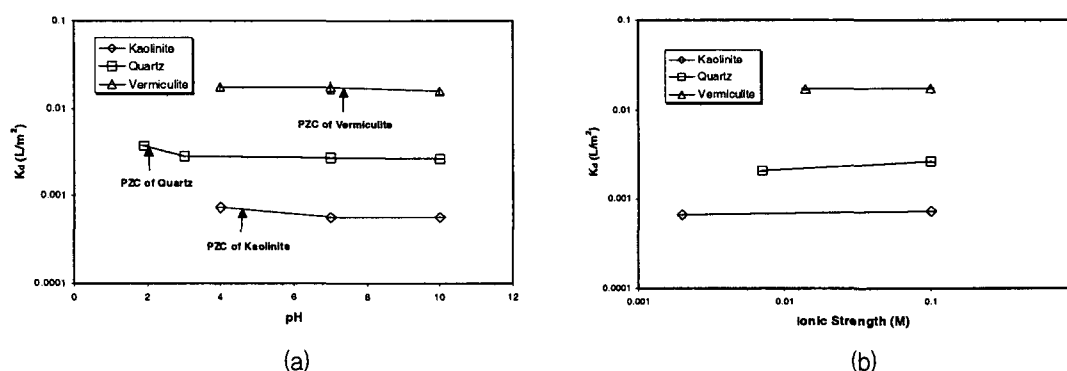


Fig. 1. The effects of pH (a) and ionic strength (b) on pyrene sorption to mineral surfaces

The effects of ionic strength on pyrene sorption to mineral surfaces were investigated and presented in Fig. 1 (b). As shown in Fig. 1 (b), ionic strength had a noticeable effect on the pyrene sorption

to kaolinite and quartz whereas salting out had little effect on the pyrene sorption to all three minerals. The salting out effect of pyrene in 0.1 M NaClO₄ salt solution was too small to affect pyrene sorption to minerals.

Effect of sorbate on PAH sorption

Fig. 2 represents the correlation between sorption distribution coefficients and aqueous activity coefficient for the sorption of the PAHs to minerals surfaces at pH = 7 and IS = 0.1 M. Fig. 2 shows that PAH activity coefficients have a strong correlation with sorption coefficients, K_d values, indicating that the hydrophobic effect of sorbate might function as one of major driving forces of PAH sorption to mineral surfaces. In addition, the different slope for three minerals in Fig. 2 suggests that sorbent chemistry (e.g., surface area and mineral type) in addition to sorbate chemistry can be of importance in determining PAH sorption behavior.

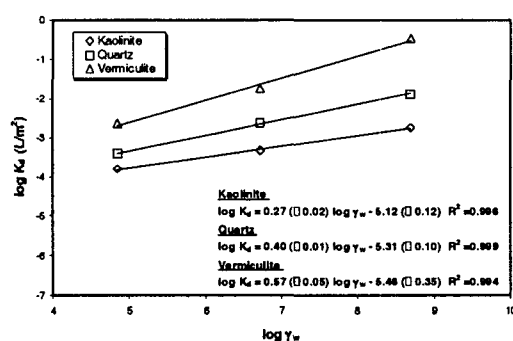


Fig. 2. Correlation between sorption distribution coefficients and aqueous activity coefficient for the sorption of the PAHs to minerals surfaces at pH = 7 and IS = 0.1 M.

Effect of sorbent on PAH sorption

If surface area is only factor determining significantly PAH sorption behavior, PAH sorption to different minerals should have same slope in Fig. 2. However, plots of log K_d versus log γ_w for the three minerals resulted in distinctly different lines, depending on the mineral type. This result suggests that mineral surface area is not only factor determining sorption behavior of HOC to mineral although it is still one of major factors affecting HOC sorption. This finding provides evidence that PAH sorption behavior is dependent on the type of mineral surface.

Fig. 3 (a) depicts the relationship between mineral surface area and PAH sorption coefficients. It is found that there is no significant correlation between surface area and PAH sorption although a general trend can be found that the sorption of two minerals except for vermiculite for a given PAH increases with increasing specific surface area of mineral. This observation indicates more clearly that surface area of mineral is not solely major factor affecting PAH sorption behavior although it can to some extent contribute to the PAH sorption to mineral surfaces.

As shown in Fig. 3 (b), there was meaningful correlation between CEC of minerals and distribution coefficients, suggesting that the mineral surface with higher CEC is more likely to provide more hospitable surface sites for PAH sorption through either way of direct interaction of exchangeable cation with PAH molecules or interaction of the favorably changed vicinal water for PAH sorption with PAH molecules.

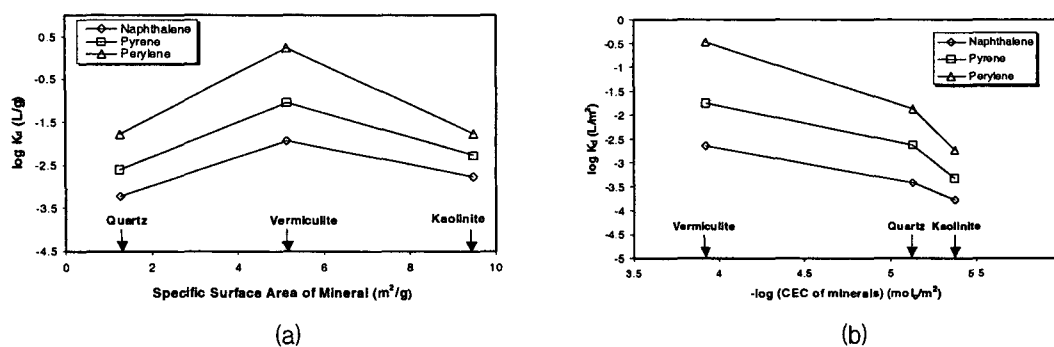


Fig. 3. Correlation between sorption distribution coefficients and mineral surface area (a), CEC (b) for the sorption of the PAHs to mineral surfaces at pH = 7 and IS = 0.1M.

4. CONCLUSIONS

The solution chemistry (i.e., pH and ionic strength) caused measurable change of PAH sorption reaction to minerals. The PAH hydrophobicity, one of sorbate chemistry, was observed to have a strong correlation with PAH sorption to mineral. It was found that the mineral surface area can to a certain extent contribute to the PAH sorption behavior to inorganic surfaces, however; it cannot be a solely factor controlling the PAH sorption. The mineral type can play a crucial role in controlling the PAH sorption behavior to mineral. The significant correlation between CEC and sorption distribution coefficients might also support that mineral surface is of much importance in controlling the PAH sorption to mineral.

5. REFERENCES

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