



Project Summary

Pollutant Sorption to Soils and Sediments in Organic/Aqueous Solvent Systems

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The solubility and sorption properties of aromatic solutes in aqueous systems containing polar organic solvents were investigated. The work addressed the situation in which the release of hydrophobic organic contaminants as a result of a spill or accidental discharge may be accompanied by the release of water-soluble organic solvents. The investigation examined the effects of a polar solvent in water on the solubility of relatively hydrophobic solutes and the effect of polar solvent-water mixtures on sorption of organic solutes onto soil. The results are interpreted by means of chemical thermodynamic models to predict solubility in water/solvent systems and by semi-empirical models to correlate reduction in sorption characteristics with increase in solubility.

This Project Summary was developed by EPA's Environmental Research Laboratory, Athens, GA, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

In recent years, several investigators have reported on measurement and modeling of the sorption of hydrophobic organic compounds onto soils. Hence, much is known about the manner in which these types of solutes sorb onto soil/sediment for the case of clean systems in which the aqueous phase contains a relatively low concentration of the organic material. This work is useful for understanding sorption and transport of organic solutes in clean water systems; however, it is not broadly applicable to

understanding organic solute sorption and transport for the case of near-source release of wastes to the environment. In these instances, the processes of solubilization, sorption, and transport of hydrophobic organic solutes may be influenced strongly by the presence of comparatively high concentrations of miscible organic solutes originating from the waste.

The phenomenon of organic solute solubilization in water co-solvent mixtures was evaluated for 18 systems. The systems were comprised of four water/co-solvent mixtures and seven solutes as listed in Table 1.

The sorption of solute onto soil in water/co-solvent systems was evaluated for two water/co-solvent mixtures (water/methanol and water/acetone), with four solutes (naphthalene, naphthol, quinoline, and 3,5-dichloroaniline), and three silt/loam soils of varying percentage fractions of organic carbon.

The solutes represented a range of physico-chemical characteristics with respect to polarity and hydrogen-bonding. The solvents represented common, water soluble solvents with different hydrogen-bonding characteristics (i.e., alcohols being either H-bonding proton donors or acceptors, and acetone being an H-bonding proton acceptor).

Results

In general, it was observed that solute solubility increased in a semi-logarithmic manner with respect to volume fraction organic solvent. For example, as shown in Figure 1, naphthalene solubility increases from approximately 31 mg/l in clean water to approximately 70,000 mg/l in 100% methanol. Data presented in Figure



Table 1. Water/Co-Solvent Systems

Methanol	Ethanol	Propanol	Acetone
Naphthalene	Naphthalene	Naphthalene	Naphthalene
Naphthol	Phenanthrene	Xylene	Naphthol
Quinoline	Aniline		Quinoline
Aniline	Xylene		3,5-Dichloroaniline
3,5-Dichloroaniline			Xylene
Xylene			
Phenanthrene			

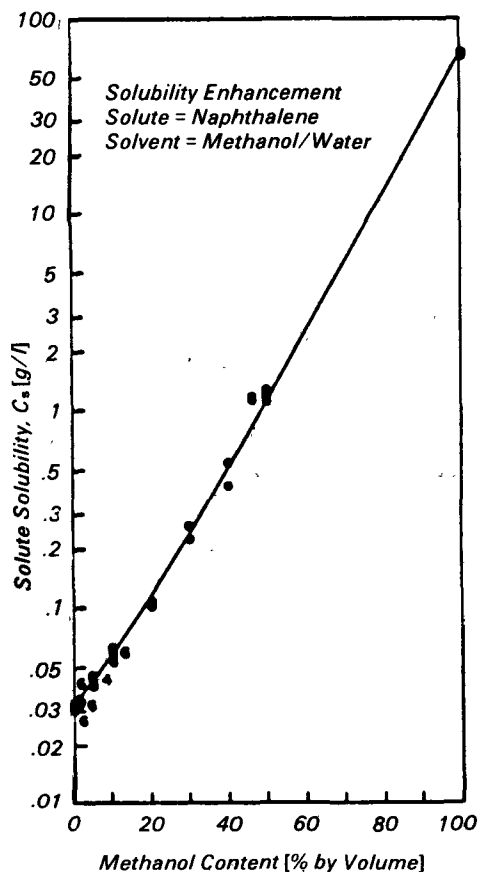


Figure 1. Naphthalene solubility in methanol/water solution.

2 show regression equations that describe the semi-logarithmic solubility behavior for four solutes and water/acetone solvent systems.

Previous work with sorption of relatively hydrophobic organic solutes onto soils/sediments has shown that sorption is inversely proportional to solubility. Thus it may be anticipated that sorption of polycyclic aromatic hydrocarbons and related compounds may decrease in a semi-logarithmic manner with respect to fraction organic solvent in the aqueous phase. This is substantiated in part by results shown in Figures 3 and 4. Figure 3 shows linear soil sorption isotherms for

naphthalene with 0, 10, 30, 40, and 50% volume fraction of acetone. The linear adsorption isotherm coefficients, K_p , for naphthalene were found to decrease semi-logarithmically with fraction acetone co-solvent. This was observed also for sorption of quinoline, naphthol and 3,5-dichloroaniline in methanol/water systems as shown in Figure 4.

Prediction of Solute Solubility

The experimental data show that the presence of an appreciable concentration of organic solvent in the aqueous phase can have a very large effect on solubility and sorption of hydrophobic organic solutes onto soils. To better understand these phenomena, several thermodynamic approaches were invoked to evaluate the solubility data. Four approaches were evaluated to predict solute solubility in water/co-solvent systems. These approaches are founded on concepts used to describe fluid phase equilibria in multicomponent systems. A brief description of each of these approaches is presented below. A thorough discussion of the results of this study and the methodologies employed for predicting solute solubility in mixed solvent systems is presented in the project report.

1. **Log-linear**—This approach follows principally from regular solution theory wherein the logarithm of mole fraction solubility is proportional to volume fraction co-solvent.
2. **Molecular Surface Area**—This approach is based on consideration of hydrophobic surface area (HSA) and polar surface area (PSA) of the solute, and interfacial free energy terms for water and solvent.
3. **Excess Free Energy**—This technique is based on expressions that describe the excess free energy that results from non-ideal mixing.
4. **UNIFAC Method**—The UNIFAC method is based on a group contribution approach for prediction of activity coefficients for solute and solvents. The method employs a

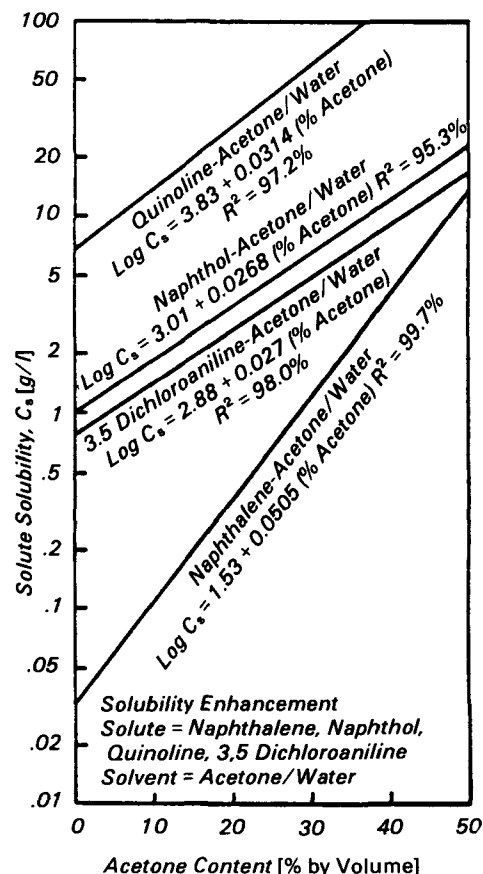


Figure 2. Solubility of naphthalene, naphthol, quinoline, and 3,5 dichloroaniline in acetone/water solution.

solution-of-group concept in which the activity coefficient is computed from parameters that relate to differences in size and shape of a molecule in a mixture and to the energy of interaction between various groups.

Prediction Results

Solubility predictions for the 18 solute/water/co-solvent systems were performed to evaluate the four approaches. In general, the UNIFAC procedure could predict solute solubility within a factor of about $\pm 50\%$. The other predictive procedures could give improved accuracy, provided sufficient experimental data were available. For most purposes, the UNIFAC procedure was suitable for initial assessment. The log-linear approach is attractive for those situations in which some solute solubility data exist for water/co-solvent mixtures.

Conclusion

Hydrophobic aromatic solutes display a semi-logarithmic increase in solubility with increasing volume fraction of co-solvent in water/co-solvent mixtures. This results in a semi-logarithmic decrease in tendency for these solutes to sorb onto soil. The increase in solubility does not result in a directly proportional decrease in sorption coefficients for the solutes studied in this investigation. The increase in solute solubility in water/co-solvent mixtures may be predicted by thermodynamic models. These predictions may be useful in other applications.

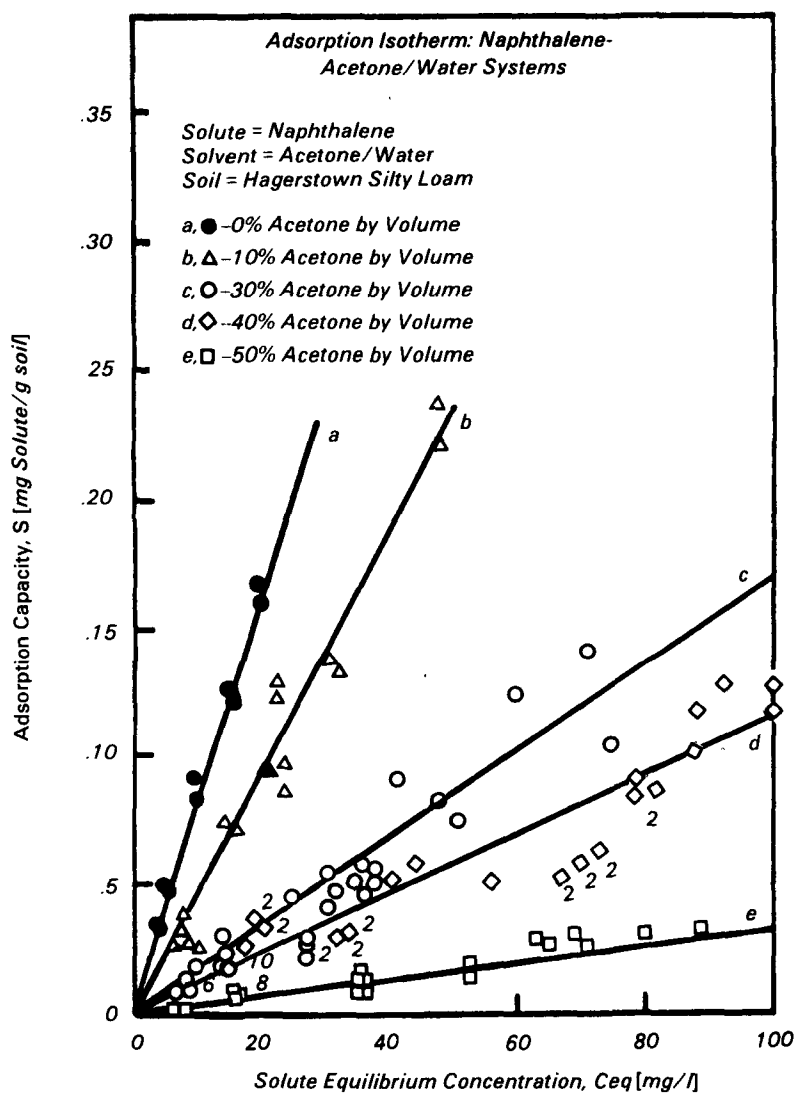


Figure 3. Naphthalene sorption to Hagerstown silt loam in acetone/water systems.

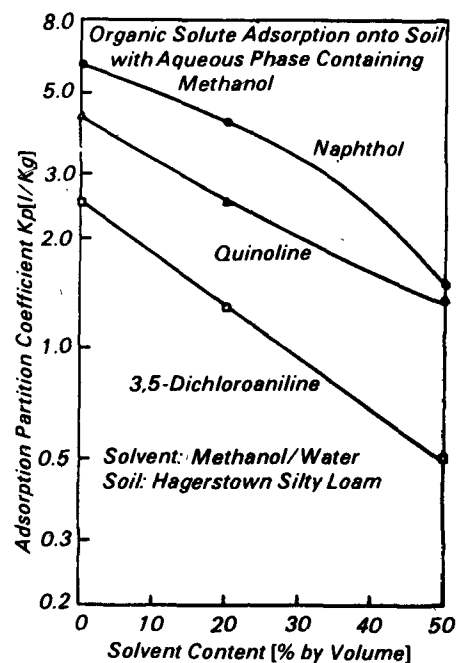


Figure 4. Sorption of quinoline, naphthol, and 3,5 dichloroaniline in methanol/water systems.

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S. W. Karickhoff is the EPA Project Officer (see below).

The complete report, entitled "Pollutant Sorption to Soils and Sediments in Organic/Aqueous Solvent Systems," (Order No. PB 85-242 535/AS; Cost: \$22.95, subject to change) will be available only from:

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