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Original article

Modelling PUF passive air samplers: Temperature dependence of polyurethane foam – Air partitioning of PAHs and their O-, N-, and S-derivatives computed by COSMO-RS

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ABSTRACT

The response of polyether-type polyurethane foam (PUF) passive samplers used to estimate the gaseous concentration of organic chemicals has been modelled using the COSMO-RS methodology. Experimental data for equilibrium partitioning ratios were used to evaluate several different oligomers as surrogates for polyurethane foam over a temperature range of 15–95 °C. Models were built with varying mole ratios of mono- or di-isocyanates and ether-based linkers derived from glycerol, ethylene oxide, propylene oxide, styrene and oligomers of ethylene oxide. Several models were found to have comparable root-mean-square (RMS) error, and COSMO-RS results were generally consistent with the empirical data. A PUF model consisting of a 1:1 condensed pair of 2,4-toluene-diisocyanide and glycerol was found to have minimal RMS error for both aromatic organic molecules and a large set of organic molecules studied between 15 and 95 °C. This model was applied to a series of simple and heteroatom-substituted polycyclic aromatics, for which the temperature dependence of air-polymer partitioning was predicted between –5 and 40 °C. Log K(PUF-Air) is found to decrease by 1.5–2.5 log units over this range, reflecting the increased volatility of the compounds with temperature, demonstrating the need for accurate exposure temperatures for partitioning involving air. The model results support the application of the passive samplers for monitoring and research studies of polycyclic aromatic compounds (PACs) in air. The approach also illustrates an efficient strategy of selective acquisition of experimental data for COSMO-RS validation, coupled by theoretical prediction of a much larger number of chemicals at various temperatures.

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1. Introduction

Environmental monitoring is a time- and labor-intensive activity that is, by necessity, spread over both large geographical areas and long periods of time. Passive sampling has emerged as a versatile tool by which to monitor large areas economically over long periods of time (Namieśnik et al., 2005; Harner et al., 2006). One approach to passive air sampling involves exposing a high surface-area polymer to large volumes of air. From the uptake kinetics of the airborne contaminant, or from its final concentration in the sampling material (assuming equilibrium is achieved), the

concentration of the contaminant in the air stream may be calculated (Shoeib and Harner, 2002; Pozo et al., 2009).

Polyurethane foam is a commonly employed passive sampling material for volatile organic chemicals such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs). For example, Harner and co-workers have employed such samplers for air-based monitoring of PCBs (Gouin et al., 2005) polyfluoroalkyl substances (PCFs) (Ahrens et al., 2013) and PAHs (Kaya et al., 2012; Schuster et al., 2015). Additionally, Galarneau et al. (2014) used results from active sampling of PAH in air using PUF to characterize emissions from oil sands tailings ponds. Work continues to characterize the uptake behavior of PUF disk samplers for PAHs and other priority chemicals in air (He and Balasubramanian, 2010; Melymuk et al., 2011; Harner et al., 2013; Bohlin et al., 2014). In all such work, the appropriate partition ratio K(PUF-Air) (also commonly referred to as partition coefficient) is required for

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computation of the contaminant concentration in the environment. Such partition ratios should apply to the temperature at which the sampling occurs, since most partitioning ratios show significant temperature dependence. Estimation of such dependence for PUF-air may be done by assuming a reasonable value for the change in enthalpy of vaporization on desorption of the impurity. The Clapeyron–Clausius equation may then be used to determine the correction needed to convert a partitioning ratio that is known at room temperature (for example) to another relevant temperature. The enthalpy change of the chemical for gaseous to sorbed states is relatively large, such that associated partition ratios show significant temperature dependence. A typical enthalpy change is 35 kJ mol^{-1} which corresponds to a typical temperature dependence of a factor of about 10 for every $50 \text{ }^\circ\text{C}$ change in temperature.

Early work on the properties of PUF as an air sampling medium were done by Bidleman and co-workers. Work by [Simon and Bidleman \(1979\)](#), [Burdick and Bidleman \(1981\)](#) and [You and Bidleman \(1984\)](#) focused on the characterization of PUF retention and break through behavior under different air flow rates and target compound vapor pressures for volatile contaminants including several PCBs and PAHs. Collection efficiencies for PUF air samplers were also reported ([Bidleman et al., 1984](#)).

The sorption properties of a variety of polymer materials have been modelled using the polyparameter linear-free-energy relationship (pp-LFER) approach of Abraham ([Abraham et al., 1995](#); [Sprunger et al., 2007](#); [Schneider and Goss, 2009](#)). This approach has proven to be very successful for chemical sorbents for which there is no experimental partitioning data. Standard errors of <0.10 log unit have been achieved for polyurethane foam by [Kamprad and Goss \(2007\)](#), making the pp-LFER approach significantly more accurate than purely theory-based approaches such as the COSMO-RS method used in this study and described below. However, this approach cannot be used with emerging contaminants for which the necessary experimental Abraham parameters (which reflect the molecular properties of acidity, basicity, polarizability, volume and excess molar refraction) have not been measured already, or cannot be measured due to lack of availability of the material in question itself. As well, [Lee and Jones \(1999\)](#) have studied the gas-polymer partitioning of polychlorinated dibenzo-p-dioxins and dibenzofurans with several field sampling media including PUF. Their experimental partitioning measurements were

correlated with several models involving experimental parameters such as correlation with vapor pressure or measured $K(\text{octanol-air})$.

In contrast to such experimentally informed approaches, relatively little has been done on the modelling of polyurethane and other polymer-based foams with purely theoretical approaches. The most successful theory-based methodology is COSMO-RS solvation theory, which is capable of treating polymeric materials such as PUF as solvation environments into which a solute can penetrate freely. COSMO-RS theory is a quantum-mechanic-based approach to predicting the physico-chemical properties of solvated molecules. The theory uses the calculated equilibrium structure, total energy and electronic charge distribution as a basis for determining the solvation energy of a molecule in different solvents. The “COSMO” (Conductor-like Screening Model) fully solvated state is used as a thermodynamic reference point, from which Gibbs energy changes may be calculated for the molecule in different solvation environments. From these energies, properties such as solubility, vapor pressure, melting and boiling points and numerous partition ratios may be calculated. Calculations are based on the interaction energy between contact segments of the solvent and solute surfaces, summed over both surfaces with weighting based on the relative probability of a given contact occurring. Thus the theory is a statistical mechanical averaging of molecular interactions to the bulk phase.

[Goss \(2011\)](#) has used the COSMO-RS methodology ([Klamt, 1995](#); [Klamt and Eckert, 2000](#)) to predict equilibrium sorption of a variety of simple neutral organics into a variety of common polymers at several temperatures between 15 and $100 \text{ }^\circ\text{C}$. This work demonstrated that good agreement may generally be achieved for partitioning from air and water to modelled polymer sorbents using the COSMO-RS approach. For polyurethane in particular, a 3:1 propylene oxide to 1,3-bis(isocyanato)benzene model was used with an RMS error of 0.46 log units at $15 \text{ }^\circ\text{C}$ and 0.34 at $95 \text{ }^\circ\text{C}$ for 101 and 89 experimental data, respectively.

The current status of COSMO-RS applications to polymer-based estimates has been summarized recently in [Loschen and Klamt \(2014\)](#), in which progress in application to estimation of vapor-liquid equilibria, polymer density, and partition ratios is reviewed in detail. Of specific interest is the fact that the RMS error associated with estimates may be reduced to about 50% by introduction of a “free-volume” entropic term in place of the conventional

Table 1
PUF model labels, codes and line structures used in this work.

| Label | Code | Composition |
|-------|-----------------------------------|--|
| 1 | 2,4-TDI:EO (1:1) | $\text{CH}_3\text{-CH}_2\text{-O-C(=O)-NH-C}_6\text{H}_3(\text{-CH}_3)\text{-NH-C(=O)-O-CH}_2\text{-CH}_2\text{-O-C(=O)-CH}_3$ |
| 2 | 2,4-TDI:PO (1:1) | $\text{CH}_3\text{-CH}_2\text{-O-C(=O)-NH-C}_6\text{H}_3(\text{-CH}_3)\text{-NH-C(=O)-O-CH}_2\text{-CH(CH}_3\text{)-O-C(=O)-CH}_3$ |
| 3 | 2,4-TDI:GL (1:1) | $\text{CH}_3\text{-CH}_2\text{-O-C(=O)-NH-C}_6\text{H}_3(\text{-CH}_3)\text{-NH-C(=O)-O-CH}_2\text{-CH(OH)-CH}_2\text{-O-C(=O)-CH}_3$ |
| 4 | 2,4-TDI:ST (1:1) | $\text{CH}_3\text{-CH}_2\text{-O-C(=O)-NH-C}_6\text{H}_3(\text{-CH}_3)\text{-NH-C(=O)-O-CH}_2\text{-CH(O-C(=O)CH}_3\text{)-C}_6\text{H}_5$ |
| 5 | 2,4-TDI:2,6-TDI:GL (1:1:1) | $\text{CH}_3\text{-CH}_2\text{-O-C(=O)-NH-C}_6\text{H}_3(\text{-CH}_3)\text{-NH-C(=O)-O-CH}_2\text{-CH(CH}_2\text{-O-C(=O)-CH}_3\text{)-O-C(=O)-NH-C}_6\text{H}_3(\text{CH}_3)\text{-NH-C(=O)-O-CH}_2\text{-CH}_3$ |
| 6 | 2,4-TDI:EO (2:2) | $\text{CH}_3\text{-C(=O)-O-CH}_2\text{-CH}_2\text{-O-C(=O)-NH-C}_6\text{H}_3(\text{-CH}_3)\text{-NH-C(=O)-O-CH}_2\text{-CH}_2\text{-O-C(=O)-NH-C}_6\text{H}_3(\text{-CH}_3)\text{-NH-C(=O)-O-CH}_3$ |
| 8 | 2,4-TDI-NCO:EO (2:2) | $\text{O=C=N-C}_6\text{H}_3(\text{-CH}_3)\text{-NH-C(=O)-O-CH}_2\text{-CH}_2\text{-O-C(=O)-NH-C}_6\text{H}_3(\text{-CH}_3)\text{-N=C=O}$ |
| 9 | 2,4-TDI-NCO:EO (2:3) | $\text{O=C=N-C}_6\text{H}_3(\text{-CH}_3)\text{-NH-C(=O)-O-(CH}_2\text{-CH}_2\text{-O)}_2\text{-C(=O)-NH-C}_6\text{H}_3(\text{-CH}_3)\text{-N=C=O}$ |
| 10 | 2,4-TDI-NCO:EO (2:3) | $\text{O=C=N-C}_6\text{H}_3(\text{-CH}_3)\text{-NH-C(=O)-O-(CH}_2\text{-CH}_2\text{-O)}_3\text{-C(=O)-NH-C}_6\text{H}_3(\text{-CH}_3)\text{-N=C=O}$ |
| 14 | 2,4-TDI-NH ₂ :EO (2:1) | $\text{O=C=N-C}_6\text{H}_3(\text{-CH}_3)\text{-NH-C(=O)-O-CH}_2\text{-CH}_2\text{-O-C(=O)-NH-C}_6\text{H}_3(\text{-CH}_3)\text{-NH}_2$ |
| 15 | 2,4-TDI-NH ₂ :EO (2:2) | $\text{O=C=N-C}_6\text{H}_3(\text{-CH}_3)\text{-NH-C(=O)-O-(CH}_2\text{-CH}_2\text{-O)}_2\text{-C(=O)-NH-C}_6\text{H}_3(\text{-CH}_3)\text{-NH}_2$ |
| 16 | 2,4-TDI-NH ₂ :EO (2:3) | $\text{O=C=N-C}_6\text{H}_3(\text{-CH}_3)\text{-NH-C(=O)-O-(CH}_2\text{-CH}_2\text{-O)}_3\text{-C(=O)-NH-C}_6\text{H}_3(\text{-CH}_3)\text{-NH}_2$ |
| G1 | 1,3-PDI-NH ₂ :PO (1:1) | $\text{CH}_3\text{-O-CH}_2\text{-CH(CH}_3\text{)-O-C(=O)-NH-C}_6\text{H}_4\text{-NH}_2$ |
| G2 | 1,3-PDI-NH ₂ :PO (1:2) | $\text{CH}_3\text{-O-(CH}_2\text{-CH(CH}_3\text{)-O)}_2\text{-C(=O)-NH-C}_6\text{H}_4\text{-NH}_2$ |
| G3 | 1,3-PDI-NH ₂ :PO (1:3) | $\text{CH}_3\text{-O-(CH}_2\text{-CH(CH}_3\text{)-O)}_3\text{-C(=O)-NH-C}_6\text{H}_4\text{-NH}_2$ |
| G4 | PI-NH ₂ :PO (1:1) | $\text{CH}_3\text{-O-CH}_2\text{-CH(CH}_3\text{)-O-C(=O)-NH-C}_6\text{H}_5$ |
| G5 | PI-NH ₂ :PO (1:2) | $\text{CH}_3\text{-O-(CH}_2\text{-CH(CH}_3\text{)-O)}_2\text{-C(=O)-NH-C}_6\text{H}_5$ |
| G6 | PI-NH ₂ :PO (1:3) | $\text{CH}_3\text{-O-(CH}_2\text{-CH(CH}_3\text{)-O)}_3\text{-C(=O)-NH-C}_6\text{H}_5$ |

Key: 2,4-TDI = 2,4-toluene diisocyanate; 2,6-TDI = 2,6-toluene diisocyanate; 1,3-PDI = 1,3 phenyl diisocyanate; PI = phenyl diisocyanate; –NCO indicates unreacted terminal isocyanates present; –NH₂ indicates hydrolysed NCO terminals present; EO = ethylene oxide; PO = propylene oxide; GL = glycerol; ST = styrene.

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