

Prediction of Vapour Pressures for Selected PCBs using the COSMO-RS Model

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Introduction

A number of computational techniques to predict the physico-chemical properties, including vapour pressure, of organic chemicals have been developed by various investigators. The Conductor-like Screening Model for Real Solvents (COSMO-RS) developed by Klamt et al.¹⁻³ is a relatively new calculational method that has been successfully used to predict vapour-liquid and liquid-liquid equilibrium data¹⁻⁵, using solely information concerning the molecular structure.

In this study, we evaluate the applicability of COSMO-RS to the prediction of the liquid phase vapour pressures of biphenyl and selected PCB congeners at temperatures ranging from 293 to 413 K. We compare these predicted values with the experimental liquid or subcooled liquid vapour pressures we previously derived from the solid vapour pressures by the Knudsen effusion method⁶ and the enthalpies of fusion and melting temperatures.

Methods and Materials

The COSMO-RS method.

A COSMO-RS calculation consists of a quantum chemical COSMO calculation based on Density Functional Theory (DFT) and the statistical thermodynamics of molecular interactions. The result of a COSMO calculation is the polarization charge density σ on the surface of the molecule in its conductor system. In this study, the software package Gaussian 03 was used for the geometry optimization and COSMO calculation.

The interaction energy of the molecules ensemble as a liquid system was derived statistically using a model that considers all possible pairs of interacting surface segments. In the statistical thermodynamic description of the molecular interactions, the polarization charge density σ was used to quantify the interaction energy of the pair-wise interacting surface segments (σ, σ'), i.e. electrostatic, hydrogen bonding and van derWaals (vdW) interactions. The chemical potential (σ -potential) of the molecules ensemble S, $\mu_S(\sigma)$, was described by the normalized distribution function of σ , $p_S(\sigma)$, which we refer to as a " σ -profile". The chemical potential of compound X in the ensemble S, μ_S^X , was derived by integrating the σ -potential of X, $p_S^X(\sigma)$ as follows

$$\mu_S^X = \mu_{C,S}^X + \int p_S^X(\sigma) \mu_S(\sigma) d\sigma \quad (1)$$

where $\mu_{C,S}^X$ is the combinatorial contribution to the chemical potential, accounting for the size and shape differences of the molecules in the system.

COSMO-RS can provide a reasonable estimation of a pure compound's chemical potential in the gas phase via;

$$\mu_{Gas}^X = E_{Gas}^X - E_{COSMO}^X - E_{vdW}^X + \omega_{Ring} n_{Ring}^X + \eta_{Gas} \quad (2)$$

where E_{Gas}^X and E_{COSMO}^X are the total chemical energies of the molecule in the gas phase and in the COSMO

conductor, respectively. The value of E_{Gas}^X was obtained from the quantum chemical calculation, and E_{vdW}^X is the vdW energy of X. The remaining contribution consists of a correction term for ring-shaped molecules, with n_{Ring}^X being the number of ring atoms in the molecule, and ω_{Ring} is an adjustable parameter. The parameter η_{Gas} provides the link between the reference states of the system's free energy in the gas phase and in the liquid.

The vapour pressure, p^X of the pure liquid component X was derived by the following equation

$$p^X = \exp\{-(\mu_{\text{gas}}^X - \mu_X^X)/RT\} \quad (3)$$

where μ_{gas}^X is the chemical potential of component X in the gas phase and μ_X^X that of the pure liquid component derived from the equation (1) (S=X). The details of the COSMO-RS theory have been presented by Klamt et al.¹ In this study, all COSMO-RS calculations were performed using the latest COSMOtherm software package, version 1.2.

Results and Discussion

In Figure 1, we compare the predicted vapour pressures of biphenyl and nine selected PCBs with experimental values at temperatures ranging from 293 to 413 K. The COSMO-RS vapour pressures agreed quite well with the experimental values for some of the PCB congeners, but consistently underestimated others. The discrepancies between the predicted and experimental values were larger for the congeners that have more chlorine substituents in the *ortho*-position, such as 2,2' substituted PCBs.

Table 1 shows the liquid phase vapour pressure results for biphenyl and the selected PCB congeners at 298 K derived from COSMO-RS. Comparing them with experimental results, we can see again that the vapour pressures from COSMO-RS seldom reflect the '*ortho*-effect', which is the tendency for the vapour pressures to be higher for congeners with more *ortho*-chlorines.⁶

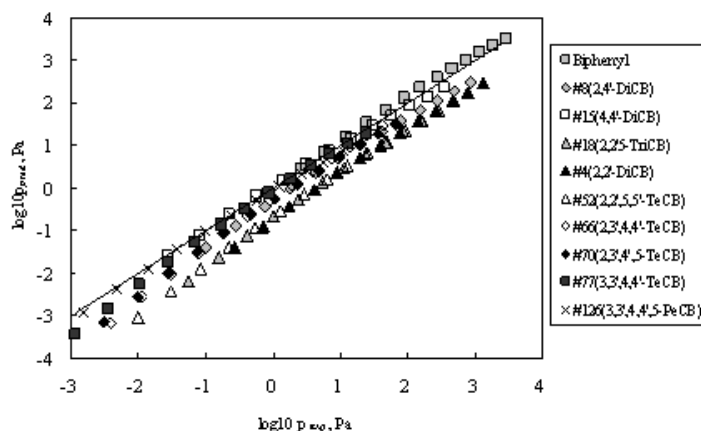
Figure 2 shows the COSMO-RS vapour pressure predictions and the corresponding experimental results for biphenyl and a subset of the PCBs at various temperatures. Although the aforementioned discrepancies exist for the congeners having more *ortho*-chlorine substituents such as 2,2' substituted PCBs, the temperature dependencies for all congeners agreed well between the experiments and predictions. It suggests that the larger disagreement between the predicted and experimental values for the more *ortho*-chlorine substituted congeners may be attributable to an error in the calculation involving the steric effect of the *ortho*-chlorine atoms.

Conclusion

We have found that the vapour pressures of PCBs predicted by the COSMO-RS method were in general agreement with experimental data. However, for the congeners with more *ortho*-chlorines, an adjustment of the combinatorial term, according for the size and shape of the molecule, in the chemical potential is necessary for accurate predictions.

Table 1. Liquid phase vapour pressures of biphenyl and selected PCB congeners at 298 K derived from the COSMO-RS method compared with our experimental values and other literature data.

Polychlorinated biphenyl (PCB) Congeners	This study		Falconer and Bidleman ⁷
	COSMO-RS	Experimental	GC-RT method
	$\log P_L$ (298 K), Pa		
Biphenyl	0.634	0.592	-
2,2'-DiCB	-1.15	-0.369	-0.485
2,4'-DiCB	-1.15	-0.783	-0.801
4,4'-DiCB	-1.45	-1.33	-1.14
2,2',5-TriCB	-1.91	-1.04	-1.11
2,2',5,5'-TeCB	-2.73	-1.76	-1.79
2,3',4,4'-TeCB	-2.87	-2.18	-2.21
2,3',4',5'-TeCB	-2.85	-2.26	-2.26
3,3',4,4'-TeCB	-3.12	-2.70	-2.66
3,4,4',5'-TeCB	-2.98	-	-2.54
2,3,3',4,4'-PeCB	-3.64	-	-3.06
2,3,4,4',5'-PeCB	-3.42	-	-2.90
2,3',4,4',5'-PeCB	-3.64	-2.77	-2.93
2',3,4,4',5'-PeCB	-3.64	-	-2.88
3,3',4,4',5'-PeCB	-3.85	-3.63	-3.31
2,3,3',4,4',5'-HxCB	-4.30	-	-3.68
2,3,3',4,4',5'-HxCB	-4.40	-	-3.70
2,3',4,4',5,5'-HxCB	-4.40	-	-3.55
3,3',4,4',5,5'-HxCB	-4.52	-	-4.18
2,2',3,4,4',5,5'-HpCB	-5.00	-4.02	-3.88
2,3,3',4,4',5,5'-HpCB	-5.04	-	-4.32

Fig. 1: Comparison of the COSMO-RS calculations (P_{pred}) with experimental values (P_{exp}).

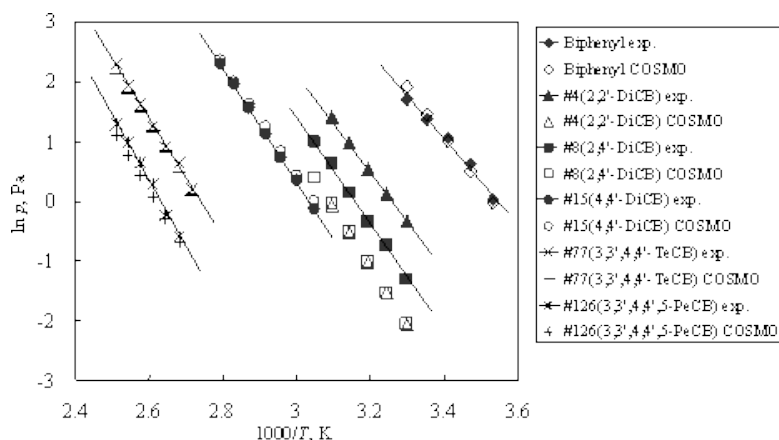


Fig.2: Comparison of the calculated and experimental vapour pressures of biphenyl and selected polychlorinated biphenyls at various temperatures.

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