

internal predictive ability ($r(cv)(2) = 0.783$). This CoMFA model was used to predict $\Delta_{fus}H(m)(T_{fus})$ of the entire set of 209 PCB congeners, including 193 PCB congeners for which experimental values are unavailable. The CoMFA-predicted values, combined with previous estimations of vaporization and sublimation enthalpies, were used to construct a thermodynamic cycle that validated the internal self-consistency of the predictions for these three thermodynamic properties. The CoMFA-predicted values of fusion enthalpy were also used to calculate aqueous solubilities of PCBs using Mobile Order and Disorder Theory. The agreement between calculated and experimental values of solubility at 298.15 K, characterized by a standard deviation of ± 0.41 log units, demonstrates the utility of CoMFA-predicted values of fusion enthalpies to calculate aqueous solubilities of PCBs.

GROUP CONTRIBUTION METHOD

In group contribution methods, solubility is assumed to be an additive–constitutive property. That is, each fragment of a molecule possesses some intrinsic solubility. Thus, solubility of a molecule can be expressed as a summation of the solubility of all the groups as

$$-\log S_w = \sum f_i \quad (3.48)$$

where f_i is the fragmental solubility constant.

Fragmental solubility constants can be determined empirically from experimental solubility data using regression techniques. In 1986, Wakita et al. (1986) studied the solubility of a large number of nonhomologous compounds in water. In this study, fragmental solubility constants were determined in the following steps:

1. Liquid aliphatic hydrocarbons were used to derive the fragmental constants by regression for some primary groups consisting of hydrogen and carbon atoms.
2. Primary group constants from step 1 were then used to determine the constants of a variety of functional groups other than hydrocarbons for liquid aliphatic compounds.
3. The aliphatic fragmental values were used to calculate the aromatic fragmental values using the solubility data of liquid aromatic compounds.
4. On the basis of the above-mentioned values, the melting point contribution was then determined for solid compounds.

The aqueous solubility of 436 aliphatic and aromatic compounds, both liquid and solid, was calculated with Equation 3.48, using fragmental solubility constants (Wakita et al., 1986). Results are shown in Equation 3.49 and [Figure 3.3](#):

$$\text{Exp. log } \frac{1}{S_w} = 0.198 + 0.917 \text{ Calc. log } \frac{1}{S_w} \quad (3.49)$$

$$s = 0.498; r^2 = 0.956; F = 10,050; n = 463$$

In an approach similar to that discussed previously, Kühne et al. (1995) determined the fragmental solubility values of 58 structure fragments and melting points for the solubility (mol L^{-1}) of 694 compounds in water. Kühne compared the performance of different methods for the calculation of solubility in water, and showed that his fragmental method resulted in the smallest calculation error.

The group contribution method has also been pursued by other researchers. Klopman et al. (1992) defined contribution values to aqueous solubility for a large set of groups and determined solubility using Equation 3.50: