

$$\ln \gamma_{iw} = a \cdot (\text{size}_i) + b$$

$$\ln C_{iw}^{\text{sat}}(L) = -c \cdot (\text{size}_i) + d$$

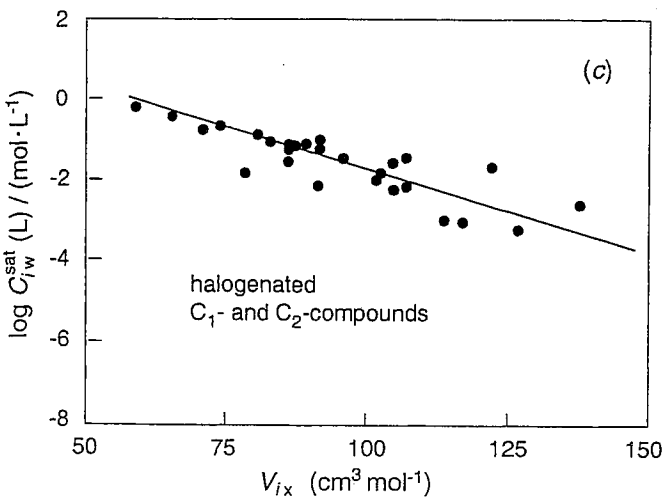
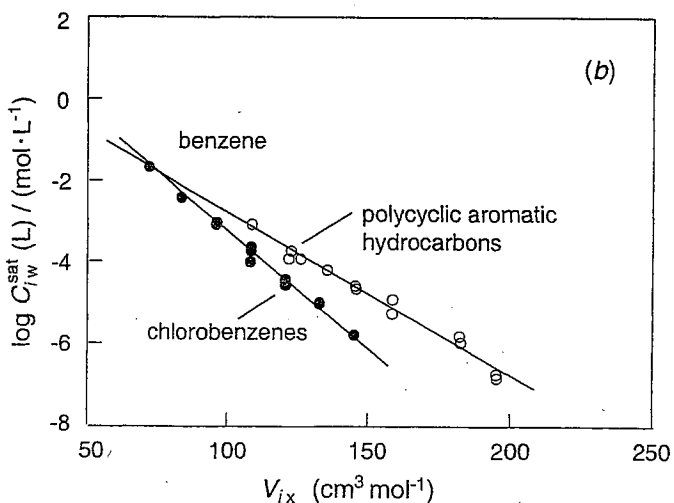
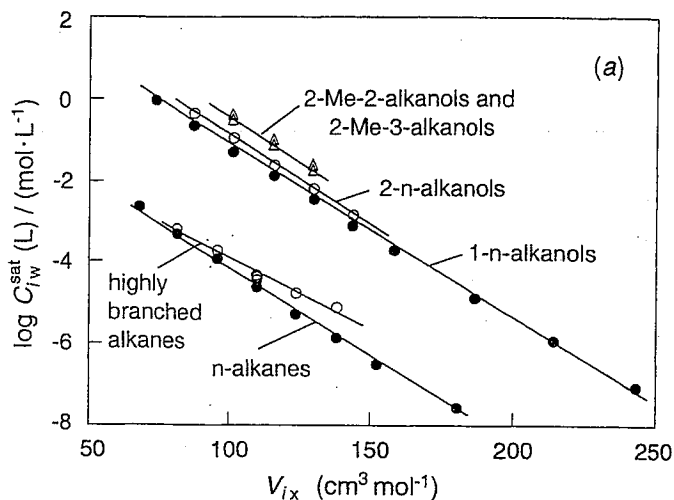


Figure 5.2 Aqueous solubility of the (subcooled) liquid compound at 25°C as a function of the estimated molar volume (V_{ix} , see Box 5.1) of the molecule for various compound classes. The linear regression equations and correlation coefficients (R^2) for the various sets of compounds are given in Table 5.4. Note that for practical reasons, decadic instead of natural logarithms are used.

(a) *n*-alkanes (C_4 - C_{16}), highly branched alkanes (C_5 - C_9), 1-3-methyl-3-alkanols (C_6 - C_8); (b) chlorobenzenes (Cl_1 - Cl_6), polycyclic aromatic hydrocarbons (benzene-benzo(a)pyrene); (c) polyhalogenated methanes, ethanes, and ethenes. Data from Appendix C and from data compilations reported by Ruelle and Kesselring (1997a and b).

$$\ln \gamma_{iw} = -\ln p_{iL}^* + s \left[(V_i)^{2/3} \left(\frac{n_{Di}^2 - 1}{n_{Di}^2 + 2} \right) \right] + p(\pi_i) + a(\alpha_i) + \quad (5-21)$$

vdW (dispersive) dipolarity/ H-donor
polarizability

+b(β_i) + vV_i + constant
H-acceptor size

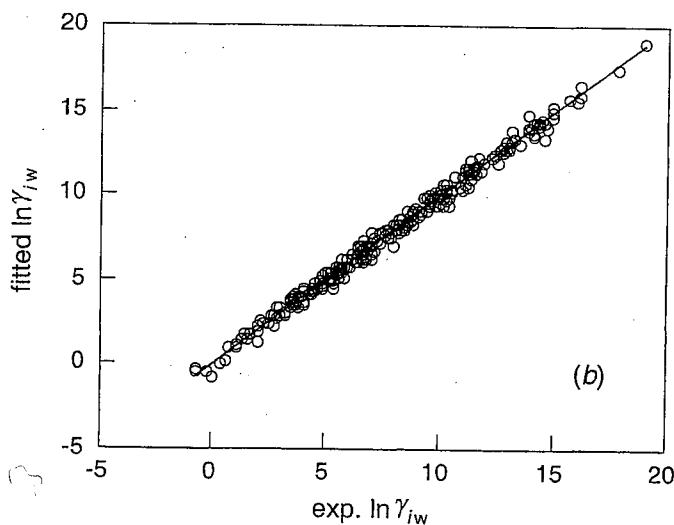
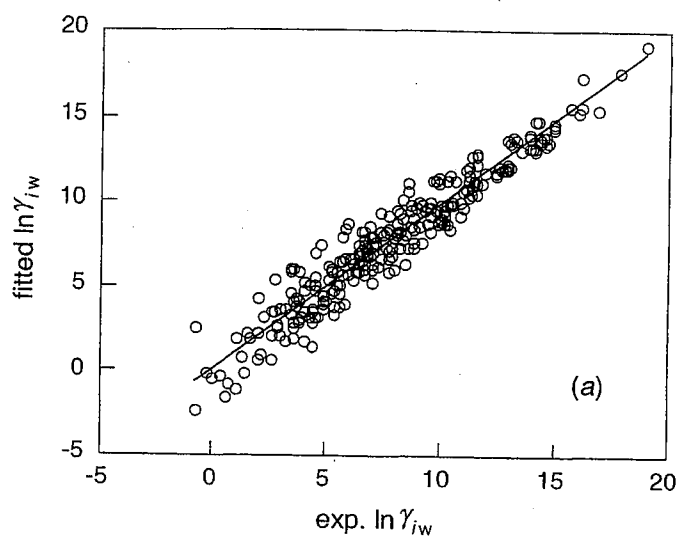


Figure 5.3 Plot of experimental versus fitted $\ln \gamma_{iw}$ values for 266 compounds covering a wide variety of compound classes. (a) Fit without using the polarizability parameter π_i (Eq. 5-20). (b) Fit including π_i (Eq. 5-21). The fitting parameters for case (b) are given in Eq. 5-22.

$$\ln \gamma_{iw} = -\ln p_{iL}^* / \text{bar} - 0.572 \left[(V_{ix})^{2/3} \left(\frac{n_{Di}^2 - 1}{n_{Di}^2 + 2} \right) \right] - 5.78 (\pi_i) - 8.77 (\alpha_i) - 11.1 (\beta_i) + 0.0472 V_{ix} + 9.49 \quad (5-22)$$

Table 5.5 Some Representative π_i Values

Compound or Group of Compounds	π_i^a	Compound or Group of Compounds	π_i^a
Alkanes	0.00	1,2,3-Trimethylbenzene	0.61
Cycloalkanes	0.10	1,3,5-Trimethylbenzene	0.52
1-Alkenes	0.08	Naphthalene	0.92
1-Alkines	0.23	Acenaphthene	1.04
Aliphatic ethers (ROR')	0.25	Chlorobenzene	0.65
Aliphatic aldehydes (RCHO)	0.65	1,2-Dichlorobenzene	0.76
Aliphatic ketones (RCOR')	0.68	1,4-Dichlorobenzene	0.75
Aliphatic carboxylic acid esters (RCOOR')	0.55-0.60	1,2,3-Trichlorobenzene	0.86
Aliphatic amines (RNH ₂)	0.35	1,3,5-Trichlorobenzene	0.73
Primary aliphatic alcohols (R-CH ₂ OH)	0.42	1,2,3,4-Tetrachlorobenzene	0.92
Secondary aliphatic alcohols (RR'CHOH)	0.36	1,2,4,5-Tetrachlorobenzene	0.86
Aliphatic carboxylic acids (RCOOH)	0.63	Benzaldehyde	1.00
Trichloromethane	0.49	Benzonitrile	1.11
Tetrachloromethane	0.38	Nitrobenzene	1.11
1,1,2,2-Tetrachloroethane	0.76	Phenol	0.89
Tetrachloroethene	0.42	Alkylphenol	0.80-0.90
Tribromomethane	0.68	2-Chlorophenol	0.88
Benzene	0.52	4-Chlorophenol	1.08
Toluene	0.52	2-Nitrophenol	1.05
1,2-Dimethylbenzene	0.56	4-Nitrophenol	1.72
1,4-Dimethylbenzene	0.52		

^a Data from Abraham et al. (1994a).

Illustrative Example 5.2

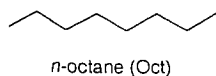
Evaluating the Factors that Govern the Aqueous Activity Coefficient of a Given Compound

Problem

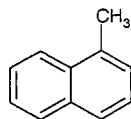
Calculate the activity coefficients as well as the excess free energies of *n*-octane (Oct), 1-methylnaphthalene (1-MeNa), and 4-*t*-butylphenol (4-BuPh) in aqueous solution at 25°C using Eq. 5-22. Compare and discuss the contributions of the various terms in Eq. 5-22.

Answer

Get the p_{iL}^* values from the data given in Appendix C. Note that 4-BuPh ($T_m = 99^\circ\text{C}$) is a solid at 25°C (use Eq. 4-40 to estimate p_{iL}^* from p_{is}^*). Calculate V_{ix} using the method described in Box 5.1. Get the n_{Di} values of the compounds from Lide (1995). Use the α_i and β_i and π_i values given in Tables 4.3 and 5.5. The resulting data sets for the three compounds are given in the margin. Recall that $G_{iw}^E = RT \ln \gamma_{iw}$. Insertion of the respective values into Eq. 5-22 yields the following result:

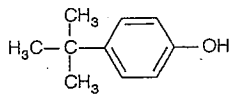


$$\begin{aligned} p_{iL}^* &= 1826 \text{ Pa} \\ V_{ix} &= 123.6 \text{ cm}^3 \text{ mol}^{-1} \\ n_{Di} &= 1.397 \\ \pi_i &= \alpha_i = \beta_i = 0 \end{aligned}$$



1-methyl-naphthalene (1-MeNa)

$$\begin{aligned} p_{iL}^* &= 8.33 \text{ Pa} \\ V_{ix} &= 122.6 \text{ cm}^3 \text{ mol}^{-1} \\ n_{Di} &= 1.617 \\ \pi_i &= 0.90 \\ \alpha_i &= 0 \\ \beta_i &= 0.20 \end{aligned}$$



4-*t*-butyl-phenol

$$\begin{aligned} p_{iL}^* &= 6.75 \text{ Pa} \\ V_{ix} &= 133.9 \text{ cm}^3 \text{ mol}^{-1} \\ n_{Di} &= 1.517 \\ \pi_i &= 0.89 \\ \alpha_i &= 0.56 \\ \beta_i &= 0.39 \end{aligned}$$

Term	Oct		1-MeNa		4-BuPh	
	$\Delta \ln \gamma_{iw}$	(G_{iw}^E) (kJ·mol ⁻¹)	$\Delta \ln \gamma_{iw}$	(G_{iw}^E) (kJ·mol ⁻¹)	$\Delta \ln \gamma_{iw}$	(G_{iw}^E) (kJ·mol ⁻¹)
$-\ln p_{iL}^*$	+4.00	(+9.9)	+9.40	(+23.3)	+9.61	(+23.8)
$-\text{vdW}^a$	-3.42	(-8.5)	-4.94	(-12.2)	-4.53	(-11.2)
$-5.78 \pi_i$	0		-5.20	(-12.9)	-5.14	(-12.7)
$-8.77 \alpha_i$	0		0		-4.91	(-12.2)
$-11.12 \beta_i$	0		-2.22	(-5.5)	-4.33	(-10.7)
$+0.0472 V_{ix}$	+5.83	(+14.4)	+5.7	(+14.3)	+6.32	(+15.7)
+ constant	+9.49	(+23.5)	+9.49	(+23.5)	+9.49	(+23.5)
$\ln \gamma_{iw} (G_{iw}^E)$	15.9	(39.3)	12.2	(30.5)	6.51	(16.2)
exp. value	16.0		12.5		7.15	

$$^a \text{ dispersive vdW} = 0.572 \left[(V_{ix})^{2/3} \left(\frac{n_D^2 - 1}{n_D^2 + 2} \right) \right]$$

First, you note that, although the three compounds are of comparable size, there are significant differences in their γ_{iw} (i.e., G_{iw}^E) values.

As is evident, the lack of any polar interactions with the water molecules is the major cause for the large hydrophobicity of Oct, although this compound exhibits the highest vapor pressure (which facilitates the transfer of Oct from the pure liquid into another phase as compared to the other two compounds). Comparison of 1-MeNa with Oct reveals that the lower activity coefficients (i.e., the higher liquid water solubilities) of aromatic compounds as compared to aliphatic compounds of similar size are primarily due to the relatively large polarizability term (π_i) of aromatic structures. Finally, from comparing 4-BuPh with 1-MeNa it can be seen that H-bond interactions (α_i, β_i terms) may decrease γ_{iw} by several orders of magnitude (note that for these two compounds, all other terms contribute similarly to the overall γ_{iw}).