New approaches for determining solubility of organic chemicals

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New approaches for determining solubility of volatile liquid chemicals

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Long-Range Research Initiative

Introduction

Water solubility is a fundamental parameter in environmental risk assessment of chemicals, and is theoretically a simple parameter to determine.

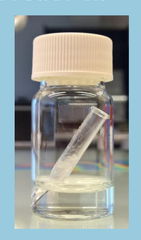
Main challenge for liquid hydrophobic chemicals:
- avoiding formation of dispersions or micro-droplets
- while establishing equilibrium within a reasonable time frame

Two new approaches were directed at solubility determinations:
1) Passive dosing from a saturated silicone polymer[1]
2) Dosing from pure phase liquid through the headspace[2]

Experimental setup

Passive dosing from saturated silicone
- Cleaned silicone rod (diameter: 3mm) was cut into pieces of 0.4 g (See A, bottom panel)
- Rods were loaded by immersion in the liquid test chemical
- Loaded rods were wiped with damp lint free tissue and rinsed three times with water
- Water was added to the loaded rods and equilibrated on a roller at 20 rpm (B & C)

Equilibration through headspace
- Glass wool was placed in glass inserts in 20 mL vials
- Liquid test chemical was added to the inserts
- Water was added to the vials
- Vials were shaken at 200 rpm, 10mm orbit for 23 hours



Test chemicals: dodecylbenzene, isopropyl myristate, hecylcyclohexane, +αPinene (D)
Analysis was done using liquid/liquid extraction with iso-octane (1-5 mL iso-octane to 5-10 mL sample) and GC-MS (E). Calibration by ^{13}C labeled standard for Dodecylbenzene and external standards for all other compounds.

Silicone loading kinetics

- Loading kinetics were determined for dodecylbenzene
- 30 rods were placed in dodecylbenzene and rolled at 20 rpm.
- At certain time steps, five rods were removed and wiped
- Swelling was determined by weight

Swelling times:
$t_{95\% \text{ of max swelling}}$ = 11 hours
$t_{99\% \text{ of max swelling}}$ = 18 hours

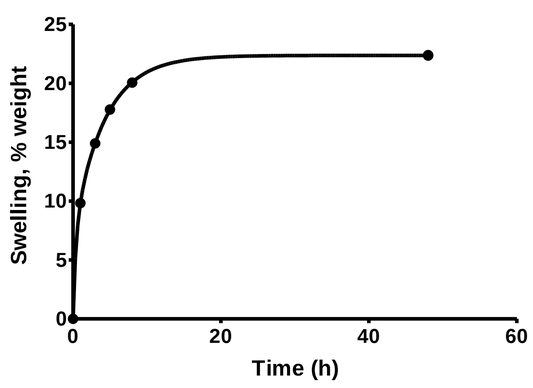


Figure 1: Swelling kinetics for 3 mm silicone rod immersed in dodecylbenzene.
Fit: First order biphasic model

Cross-validation

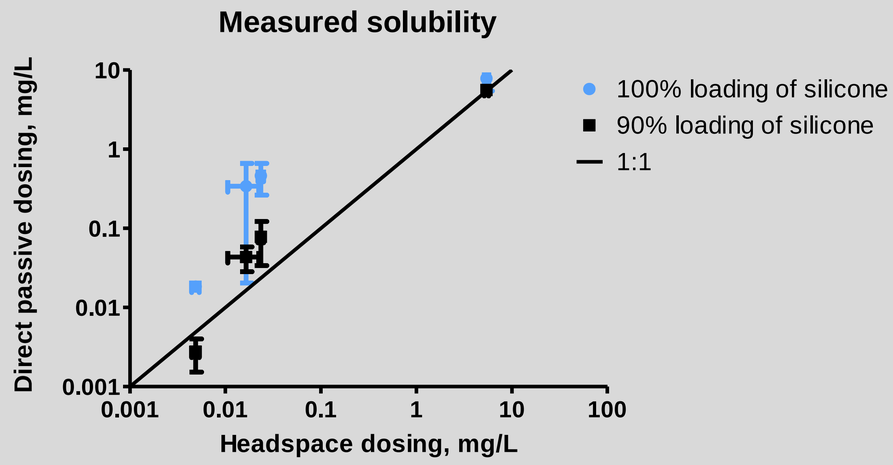
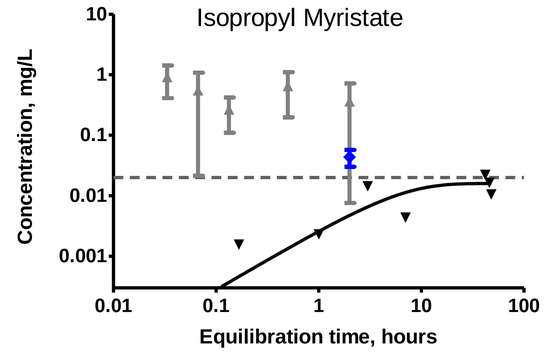
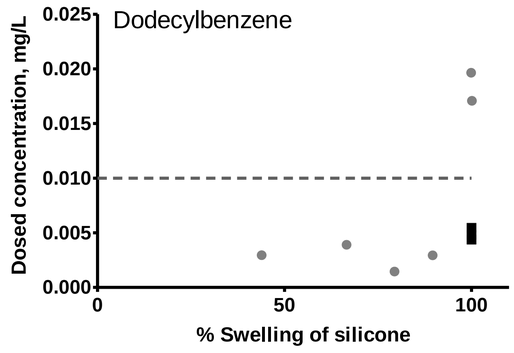


Figure 4: Solubility measured by direct passive dosing from 100 and 90% swelling of silicone as a function of solubility measured by headspace dosing. Mean and s.d., n=3

Generating saturated solutions





100% Direct passive dosing | Headspace equilibration | Direct passive dosing | Headspace
EpiSuite estimated solubility | 90% Direct passive dosing | EpiSuite experimental database

Figure 2: Equilibrium kinetics for direct passive dosing and headspace dosing of isopropyl myristate. Mean and s.d.

Figure 3: Direct passive dosing of dodecylbenzene from silicone rods loaded at varying swelling percentages

Conclusion

- Saturation of 3 mm silicone rod by swelling can be obtained within one day
- Direct passive dosing at 90% swelling agreed with headspace equilibrated solubility measurements
- Direct passive dosing at 100 % swelling produced markedly higher concentrations than headspace equilibration and direct passive dosing at 90 % swelling – third phase challenges
- Headspace dosing is a promising method for solubility determinations for volatile liquid chemicals
- Direct passive dosing for solubility measurements of hydrophobic chemicals requires further work

References: [1]Stibany, F., Schmidt, S.N., Schäffer, A. and Mayer, P. 2017. Aquatic toxicity testing of liquid hydrophobic organic chemicals – passive dosing exactly at the saturation limit. Chemosphere 167: 551-558.
[2]Trac, L.N., Schmidt, S.N and Mayer, P. Submitted. Headspace passive dosing of volatile hydrophobic chemicals – aquatic toxicity testing exactly at the saturation level.
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