



Determination of the solubility of low volatility liquid organic compounds in water using volatile-tracer assisted headspace gas chromatography



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ABSTRACT

This study reports a new headspace gas chromatographic method (HS–GC) for the determination of water solubility of low volatility liquid organic compounds (LVLOs). The HS–GC analysis was performed on a set of aqueous solutions containing a range of concentrations of toluene-spiked (as a tracer) LVLOs, from under-saturation to over-saturation. A plot of the toluene tracer GC signal vs. the concentration of the LVLO results in two lines of different slopes that intersect at the concentration corresponding to the compound's solubility in water. The results showed that the HS–GC method has good precision (RSD <6.3%) and good accuracy, in which the relative difference between the data measured by the HS–GC method and the reference method were within 6.0%. The HS–GC method is simple and particularly suitable for measuring the solubility of LVLOs at elevated temperatures. This approach should be of special interest to those concerned about the impact of the presence of low-volatility organic liquids in waters of environmental and biological systems.

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Nomenclature

H	vapor-liquid equilibrium partition coefficient
K	Solid-liquid distribution constant
C_g	concentration of the volatile species in vapor phase
C_a	concentration of the volatile species in liquid phase
C_d	concentration of the volatile species in solid phase
V_g	the volume of the vapor phase
V_a	the volume of the liquid phase
V_d	the volume of the solid phase
V_o	the total volume of LVLO added
V_s	the volume of saturated liquid phase
m	the mass of the tracer in the original sample
w	concentration of LVLO
w_s	the concentration of saturated LVLO
k	proportionality coefficient
ρ	density of LVLO
S_1	slope of the unsaturated solution
S_2	slope of the saturated solution

1. Introduction

The solubility of an organic liquid in water fundamentally depends on the physical and chemical properties of the organic solute, as well as on the temperature, pressure and the polarity of the solute and solvent molecules [1]. This solubility is important in a variety of investigations on the behavior and effects of these compounds in aqueous media. For example, the widespread production and use of natural and synthetic organic materials in today's world have resulted in the contamination of valuable surface and subsurface water resources through events such as oil spills, leaking underground storage tanks and pipelines, and leaching from hazardous waste sites [2,3]. Although the aqueous solubility of the organic contaminants is usually very low, it is often large enough to seriously degrade water quality and pose threats to the environment and human health [4,5]. Due to the low volatility, these organic compounds remain more likely in the water system and thus create biological problems in humans and the environment. Therefore, in many areas of research (e.g., in the modeling of their environmental transport and fate properties) it is important to have a fast and reliable method to estimate the solubilities of the low-volatility liquid organic compounds (LVLOs, i.e., with the initial boiling point greater than 250 °C) in water.

The conventional method for measuring the solubility of an organic compound in water involves a long, complex procedure that is based on preparing, equilibrating, and analyzing a saturated aqueous solution of the solute [6–8]. In addition to the problem of the limit of detection of the analytical method used, there is a major difficulty in maintaining a constant temperature during the entire procedure from sample preparation to analytical measurement. As a result, there is a possibility that significant variations could occur when determining the solubility using these methods. For example, the solubility of styrene in water at 60 °C has been reported as 0.053% and 0.96% by two different groups [9,10]. Because of these difficulties, there is a lack of solubility data on many organic compounds available in the literature, particularly solubilities at temperatures above room temperature, e.g., those met in the emulsion polymerization [10,11].

In general, headspace (HS) analysis is a technique based on vapor-liquid equilibrium (VLE) in a sealed vial at a given temperature. By measuring the volatile solute partially released from the liquid sample, the content of the volatile solute in the original sample solution can be indirectly determined [12]. Gas chromatograph (GC) is a typical instrument incorporated in HS analysis for

quantifying the content of the analyte(s) in the vapor phase. One of the advantages of HS-GC is that the measurement for the volatile species is performed *in situ* thereby eliminating errors associated with temperature changes occurring in the sampling and analysis in the conventional method. Previously, we successfully developed a multiple headspace extraction (MHE) GC technique to determine the solubility of volatile organic monomer in water [13]. In this method, a volatile monomer (slightly over-saturated) solution was prepared in a closed sample vial, which is a three-phase system that including the vapor phase, aqueous phase, and monomer droplet phase. The excess amount (i.e., the droplet phase) of the monomer in the headspace sample vial is step-wisely reduced at each headspace sampling, by venting the vapor monomer from the vial, during MHE. After the excess amount of the monomer is completely removed from the solution, a transition point is observed when plotting GC signals vs. the MHE numbers. The vapor content of monomer at this transition point is related to its solubility in water. Therefore, the solubility of the monomer in water can be determined through a proper calibration procedure. However, because there is very low or no signal in the vapor phase to be detected for the solutes with low or non-volatility in water, such HS-GC method can not be used to measure the solubility for these compounds. Moreover, a calibration procedure for quantifying the vapor analyte content in HS-GC measurement is required, which makes the method not only complicated but also time-consuming. Recently, we have applied the MHE-GC method to the determination of the viscosity of a liquid, utilizing a volatile species in the liquid as a tracer [14]. Based on kinetically monitoring the changes of the volatile tracer in the vapor phase, the relationship between the rate of volatile tracer released from the liquid and the viscosity of the liquid can be established.

In this paper, we adopted the concept of volatile tracer from the above work to present a new, simpler, more accurate method for determining the solubility of low volatility liquid organic compounds (also including non-volatile organic species) in water. Because of the *in-situ* sampling in the equilibrated system in headspace auto-sampler, this new method overcomes the problem of the temperature changes met in the conventional methods reported previously. The major foci of this work have been on establishing the methodology, selecting the volatile tracer, and determination of the best conditions for the phase equilibrations in the sample system.

2. Experimental

2.1. Samples

All chemicals used in the experiment were analytical grade purchased from Sigma-Aldrich, including methanol (purity > 99.5%), toluene (purity > 99.8%), triacetin (purity > 99.8%), caprylic acid (purity > 99.5%), oleate (purity > 99.4%), hexyl acetate (purity > 99.5%) and nitrobenzene (purity > 99.8%). A 1% by volume toluene-methanol solution was prepared by adding 0.1 mL of toluene to 10 mL of methanol.

2.2. Apparatus and operations

HS-GC measurements were carried out with an automated headspace sampler (DANI HS 86.50, Italy) and a GC system (Agilent GC 7890A, US) equipped with a flame ionization detector and a DB-5 capillary column (30 m × 0.32 mm × 0.25 μm) from J&W Scientific, US, operating at the constant temperature (80 °C) and nitrogen carrier gas flow rate (3.8 mL/min). Headspace operating conditions were as follows: strong shaking for equilibration of the sample at the desired temperature; pressurization pressure = 2.00 bar; carrier

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