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Short communication

Simplified multiple headspace extraction gas chromatographic technique for determination of monomer solubility in water

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Abstract

This paper reports an improved headspace gas chromatographic (GC) technique for determination of monomer solubilities in water. The method is based on a multiple headspace extraction GC technique developed previously [X.S. Chai, Q.X. Hou, F.J. Schork, J. Appl. Polym. Sci., in press], but with the major modification in the method calibration technique. As a result, only a few iterations of headspace extraction and GC measurement are required, which avoids the "exhaustive" headspace extraction, and thus the experimental time for each analysis. For highly *insoluble* monomers, effort must be made to minimize adsorption in the headspace sampling channel, transportation conduit and capillary column by using higher operating temperature and a short capillary column in the headspace sampler and GC system. For highly water *soluble* monomers, a new calibration method is proposed. The combinations of these technique modifications results in a method that is simple, rapid and automated. While the current focus of the authors is on the determination of monomer solubility in aqueous solutions, the method should be applicable to determination of solubility of any organic in water.
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1. Introduction

Recently, we have developed a multiple headspace extraction (MHE) gas chromatographic technique for determination of monomer solubility in water system [1]. The concept of this new technique is to place a two phase mixture of monomer and water in a closed headspace sample vial, and then use MHE (replacing the extracted vapor with inert gas) to gradually remove the excess monomer from the vial. Since the equilibrium vapor concentration decreases dramatically at the point at which monomer is no longer present as a separate phase, a transition point in the profile of headspace extraction number versus vapor monomer concentration measured by headspace GC can be determined. This transition point corresponds to the monomer saturation point in the aqueous solution, i.e., its solubility in water.

Since the equilibration temperature can be precisely controlled in the commercial headspace sampler system, and the GC can conduct a precise headspace sampling, the results from this method is very accurate and reproducible. Based on this novel technique, we conducted solubility measurements on a set of vinylic monomers at a temperature of 60 °C [2]. In order to efficiently obtain the transition point in MHE process, it is best to add just a slight excess of monomer in water (beyond its solubility in water, thus forming a small volume of separate monomer phase). However, this can be difficult if the solubility of the monomer is not known at least approximately. As a result, it is often necessary to add a large excess of monomer, and then to run a large number of headspace extractions to reach the transition point; this can consume a great deal of analysis time. Highly water soluble monomers present an additional problem in calibration because the calibration is based on Henry's law, which is no longer valid if the monomer is very soluble.

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In this work, we reported an improved headspace gas chromatographic (GC) technique for determination of monomer solubilities in water based the multiple headspace extraction GC technique which avoids these problems. The method is simple, rapid and practical.

2. Experimental

2.1. Chemicals

The monomers used in this work were obtained from commercial sources. Deionized water was used in the sample preparations.

2.2. Experimental apparatus

All measurements were carried out using an HP-7694 automatic headspace sampler and Model HP-6890 capillary gas chromatograph (Agilent Technologies, Palo Alto, CA, USA). GC operating conditions were as listed in the previous paper [1].

3. Results and discussion

3.1. MHE GC method

Fig. 1 shows the profiles of vapor monomer concentration versus headspace extraction number in three styrene–water solutions, in which the solutions contain the same (excess) amount of styrene but different amount of a surfactant (TX-100). Eq. (1) is used for calculating monomer solubility in the previous work [1] (Fig. 1).

$$C_x = \frac{A_{t+1} - bA_{t+2}}{a} C_0 \tag{1}$$

where the factors a and b are obtained by curve fitting based the MHE GC measurement on a standard solution in the cal-
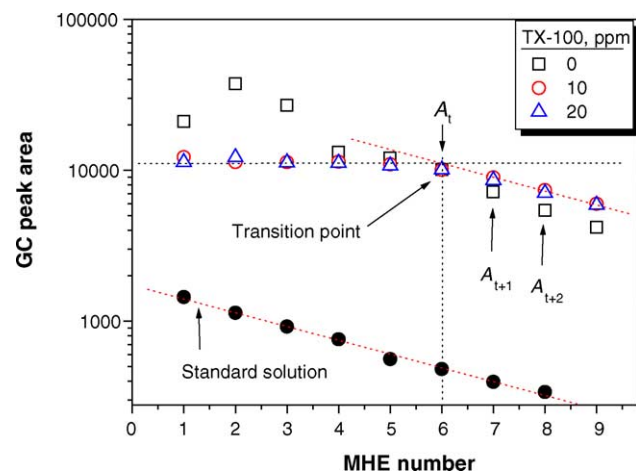

Fig. 1. Vapor methyl methacrylate content profiles during MHE process.

Table 1
Symbols and definitions

A_{t+1}	GC peak area at the extraction number after the transition point, t
A_{t+2}	GC peak area at the extraction number after the $t+1$ point
$\sum_{1}^{n-1} A_i$	Sum of GC peak areas from headspace extraction number 1 to $n-1$
A_n	GC peak area at headspace extraction number n (=1, 2, ..., n), $A_n = kC_g^n$
A_0	GC peak area of the standard solution
C_0	Monomer concentration in the standard solution
C_x	Monomer solubility in water
C_g	Equilibrated vapor monomer concentration
C_l	Equilibrated monomer concentration in the water phase
C_g^0	Equilibrated vapor monomer concentration of the standard solution
k	GC response factor
H	Dimensionless Henry's law constant
V_g	Volumes of vapor phase
V_l	Volumes of liquid phase

ibration, i.e.,

$$\sum_{i=1}^{n-1} A_i = a + bA_n \tag{2}$$

All symbols are defined in Table 1.

As noted above, in order to obtain A_{t+1} and A_{t+2} (as shown in Fig. 1), an "exhaustive" numbers of headspace extraction may be required when an arbitrary excess of monomer is added, due to a lack of knowledge of even the approximate monomer solubility.

3.2. Importance of surfactant

In absence of surfactant, as shown Fig. 1, there is a good deal of scatter in the initial MHE GC measurement on a solution with an excess of styrene. This is often the case for monomers with a low specific gravity and relative high solubility. Therefore, several headspace extractions are necessary to remove the excess monomer from the system. Thus, the data obtained from initial headspace measurement is not reliable and useless in the solubility determination. However, this problem can be greatly overcome by adding a small amount of surfactant into the test mixture. As shown in Fig. 1, a small amount of surfactant (TX-100) is very effective in stabilizing the monomer droplets in the solution when an excess of monomer is added. As a result, the agglomeration of the monomer droplets can be prevented, which reduce the risk of the large monomer droplets (with a lower specific gravity than water) floating to the surface of the mixture clinging to the walls of the sample vessel. Thus, an equilibrated vapor monomer content on this saturated solution can be obtained with few MHE GC measurements. As noted by Anderson [3], the small amount of surfactant does not normally affect the solute vapor–liquid equilibrium (VLE). However, we suspect that the presence of even a small amount of surfactant may change the VLE behavior of highly insoluble monomers. In

such a case, the surfactant-free solution in testing is recommended.

The equilibrated vapor monomer concentration corresponds to the saturated monomer concentration (i.e., the solubility in water) if monomer droplets remain in the liquid phase. However, a standard solution cannot simply be applied for the calibration without precaution because a vapor–liquor re-equilibration takes place when it is placed in a closed sample vial. As a result, the monomer concentration in the solution becomes unknown although its vapor concentration can be determination by GC.

3.3. A simple calibration technique

The conventional calibration technique as reported by Kolb and Ettre [4] cannot be simply applied to this work without precaution. The key issue is how to avoid a significant mass loss of the monomer in the standard solution during the VLE, so that a calibration based unsaturated standard solution for a saturated unknown solution is valid.

As it is known that in a closed-system, the total mass of solute ($m_0 = C_0 V_1$) in the standard (original) mixture is the sum of the masses in the vapor ($m_g = C_g V_g$) and liquid ($m_1 = C_1 V_1$) phases in the closed system, i.e.,

$$C_0 V_1 = C_g V_g + C_1 V_1 \qquad (3)$$

For an unsaturated solution, and monomer with a low solubility, the VLE equilibration can be considered a diluted system and described by Henry's law, i.e.,

$$H = \frac{C_g}{C_1} \qquad (4)$$

Combining Eqs. (3) and (4), the monomer concentration ratio of the liquid phase in the sample vial after equilibration to the standard (original) solution can be expressed as:

$$\frac{C_1}{C_0} = \frac{V_1}{HV_g + V_1} \qquad (5)$$

If $HV_g \ll V_1$, $C_1/C_0 \rightarrow 1$, i.e., $C_1 \rightarrow C_0$. Thus, the monomer concentration of the liquid phase in the sample vial after equilibration is nearly the same as that in the standard (original) solution. Therefore, a simple calibration method can be applied using Henry's law (Eq. (4)), i.e.,

$$\frac{C_g}{C_s} = \frac{C_g^0}{C_0} \qquad (6)$$

Since GC peak area (A) is linearly proportional to the vapor concentration, i.e., $A = kC_g$. Eq. (6) can be written as,

$$\frac{A_x}{C_x} = \frac{A_0}{C_0} \qquad (7)$$

or

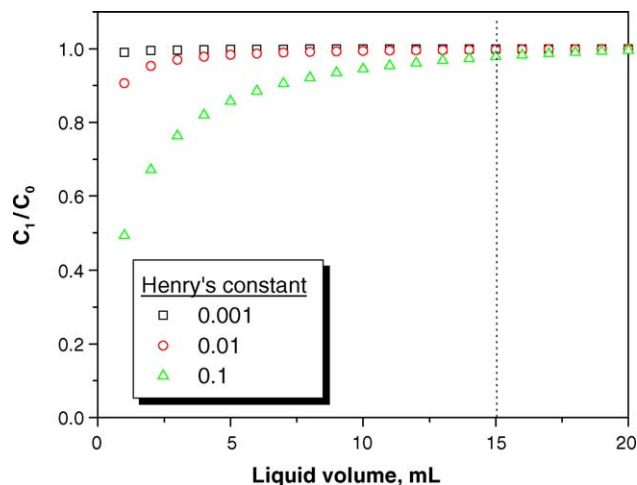$$C_x = \frac{C_0}{A_0} A_x \qquad (7a)$$

Fig. 2. Relationships between monomer molar ratio and liquid volume at different Henry's law contents.

The total volume ($V_t = V_g + V_1$) of the sample vial used in the commercial headspace GC system is about 20 mL. The dimensionless Henry's law constants for most monomers are very small. For example, the Henry's law constant of MMA at 60 °C is about 0.01; thus a sample liquid size of 5 mL is sufficient to ensure that the monomer concentration change in the liquid phase is negligible (less than 2%). Fig. 2 shows the relationship between the molar ratio (C_1/C_0) and the liquid size in a given volume of sample vial (20 mL) for the species with the dimensionless Henry's law constants of 0.001, 0.01 and 0.1, respectively.

Clearly, for a given monomer species (i.e., its Henry's law constant is known), $C_1/C_0 \rightarrow 1$, can be achieved by using a larger liquid volume. The liquid volumes greater than 15 mL in the current headspace GC system can cause the problem in headspace sampling because the liquid immerses the sampling needle inlet. However, it can be easily solved using a vapor-well proposed in the previous work [5].

3.4. Method validation

There are limited dada of monomer solubility at an elevated temperature. Also, the solubility at higher temperate reported in the literatures are often inconsistent, e.g., the styrene solubility date at 60 °C were reported totally different from two separate references [6,7], one is 0.053% and other is 0.96%. However, the monomer solubility at a room temperature from different sources matches well. Therefore, the method validation in the present work was conducted based on both styrene and methyl methacrylate solubility data at a 25 °C. The solubility data obtained by the present method are 1.53% for methyl methacrylate and 0.032% for styrene, respectively, which agree well with those reported in the literature [8].

It should be pointed out that the current headspace sampler cannot conduct a equilibration at a room temperature due to a lack of cooling system. In this work, we used

an external compressed air to cool the headspace oven to 25 °C.

3.5. A calibration method for highly soluble monomers

If the monomer is very soluble, the interaction between the monomer molecules cannot be neglected when its concentration in water is very high. Thus, Henry's law is no longer valid and therefore one cannot simply use Eq. (7a) in the calibration. At a higher concentration, the VLE partition coefficient of the monomer is non-linear that is dependent on the monomer concentration in the aqueous phase. Thus, multiple standard solutions with different monomer concentrations that are close to its solubility are required in the calibration.

Acylonitrile is a very soluble monomer with a solubility of 7.9% in water at a room temperature. In the present study, a set of acrylonitrile standard solutions was prepared with a concentration of 0–10% (weight base). The solutions are clear at a room temperature after strong shaking and equilibration to ensure that the monomer is completely dissolved in water. These solutions were placed to the headspace sampler at a temperature of 60 °C, the equilibrated vapor contents were measured by GC, which are shown in Fig. 3.

In this figure, a non-linear relationship between the vapor concentrations and the liquid concentration of the monomer is observed. However, a linear relationship between $A^{1.22}$ and monomer concentration, C, in the standard solutions can be built-up, i.e.,

$$A^{1.22} = kC \tag{8}$$

By MHE GC measurements on a solution with an excess amount of acrylonitrile at 60 °C, the GC peak area, i.e., the equilibrated vapor acrylonitrile content on this saturated solution was obtained. Acrylonitrile solubility was then calculated according to Eq. (8). The solubility of acrylonitrile in water at 60 °C obtained by the present method is 10.3%,
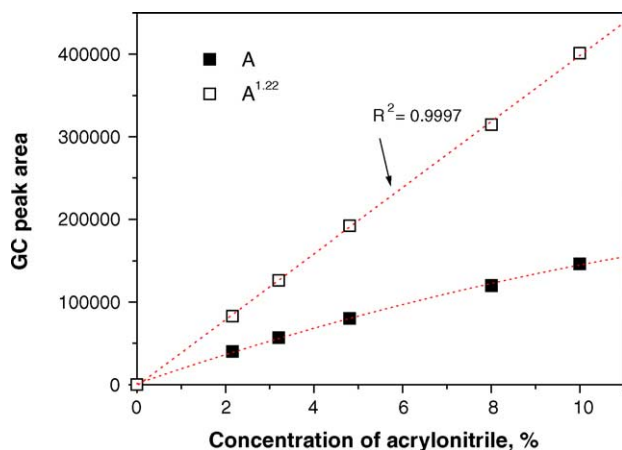
which matches the literature value of 11.0 at 60.3 °C reported for a turbidity method [7]. It indicates that the present headspace GC method is also applicable for the solubility determination of very soluble monomers.

It should be noted that the exponent in Eq. (8) will be different for different monomers. Since the very soluble monomers are usually more volatile, small sample loop or inlet split mode should be applied to locate the GC response on headspace measurement within a linear range.

3.6. Aspects in the solubility measurement for very insoluble monomers

If a monomer is too insoluble in water, it will be difficult to measure. Because the mixture only contains a very small amount of dissolved monomer a very low vapor concentration in the headspace is measured. The adsorption effect of vapor monomer on the headspace-sampling channel, transportation conduit to GC system will be very significant. Moreover, the very insoluble monomers usually have a strong retention on the GC column (such as HP-5), which leads to a significant tailing in GC chromatogram that makes the signal undetectable or adds significant error to the measurement. In order to minimize these problems, the high operating temperature (>110 °C) in headspace sampling and transportation system was chosen. Since the separation is not required in single monomer solubility determination, a very short capillary column (e.g., a length of 0.5 m or shorter) can be used as a conduit connecting to GC FID detector. With such modifications in instrument and operation parameters, we were able to determine the monomer solubility as low as 10^{-4}% [2].

4. Conclusions

An improved headspace gas chromatographic technique for determination of monomer solubilities in water has been developed. It greatly simplifies the calibration procedures. A new calibration method is proposed for the solubility determination of highly water soluble monomers. For highly water insoluble monomers, efforts must be made to minimize the adsorption problem in the headspace sampling channel, transportation conduit and capillary column by using a higher operation temperature and a short capillary column.

The present method is simple, rapid and automated. It is practical for the determination of monomer solubility over a wide range.

Fig. 3. Signals of GC headspace measurement vs. the concentrations of acrylonitrile in water.

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