Determination of the Solubility of a Monomer in Water by Multiple Headspace Extraction Gas Chromatography

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ABSTRACT: In water-based polymerization (suspension, microsuspension, emulsion, miniemulsion, and microemulsion polymerization), the solubility of the monomer in the aqueous phase can have profound effects on the final polymer product. This article demonstrates a novel method for the determination of monomer solubility in water with headspace gas chromatography (GC). In this method, an excess amount of an organic solute of interest was added into a closed headspace vial containing a given volume of water. The organic solute and water in the vial was well mixed by strong hand shaking; then, the equilibrated vapor solute in the vial at a desired temperature was measured by headspace GC with a multiple headspace extraction mode. In each headspace extraction, a part of the vapor phase in the vial was vented for GC analysis and replaced with an inert gas. The excess amount of solute in aqueous solution was eventually removed from the vial after multiple headspace extractions, and the solute concentration in water reached its saturation point. After that point, the concentration of the solute in the vapor dramatically decreased in each subsequent headspace extraction. By plotting vapor concentration versus headspace extraction number, we determined the transition point. The vapor concentration at this point corresponded to the solute solubility, which was calculated through a calibration. This method was very simple and automated; it could easily be used for organic solute solubility measurement at an elevated temperature. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 1296–1301, 2006

Key words: monomers; chromatography

INTRODUCTION

In water-based polymerization (suspension, microsuspension, emulsion, miniemulsion, and microemulsion polymerization), the solubility of the monomer in the aqueous phase can have profound effects on the final polymer product. Unfortunately, monomer solubilities in water are often unavailable. Solubility analyses are often complex and time-consuming, and results are inaccurate. In addition, the results from different analytical techniques are difficult to compare. The traditional method for the determination of organic solubility in an aqueous solution is based on the analysis of an aqueous solution saturated with the solute in question. This aqueous solution can be prepared by the equilibration of an organic solvent with water. At equilibrium, the solute concentration is at its saturation value. Through the determination of the solute concentration in the aqueous solution, the solubility can be obtained. However, this procedure is very time-consuming because the analysis of the aqueous phase can be only performed after a two-phase equilibration is achieved and complete phase separation has occurred. Moreover, there are also sampling difficulties if the solubility data is desired at an elevated temperature, in which a two-phase equilibrium change takes place because of a different temperature in the sampling device.

A turbidity-like method was reported for determination of the solubility of styrene in water in 1946.[1,2] In the method, the styrene solubility measurement is based on the observation of the so-called cloud-point formation by the direct addition of the known amount of monomer into water[1] or in an unsaturated, monomer-containing, aqueous solution during the temperature decrease.[2] The cloud point is formed when the monomer concentration is oversaturated. Obviously, such an experimental procedure can easily cause larger human error through visual cloud-point observation. Although this may overcome with a turbidometer, good uniformity in the studied solution system is very difficult to achieve. As a result, significant differences in solubility measurement have been presented; for example, styrene solubility at 60°C has been reported as 0.053%[1] and 0.96%,[2] respectively, from two separated groups.

Although gas chromatography (GC) can provide good quantification analysis for most monomers, its

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application in monomer solubility study is limited because of the difficulties in solution equilibration and sampling, as mentioned previously. Headspace GC has been used in the determination of volatile organic compounds (VOCs) and the study of their vapor–liquid equilibration (VLE). In a previous work, we developed several methods for the determination of VOC VLE partition coefficients on the basis of a commercial headspace GC system.[3,4] We also reported an indirect method for the determination of the solubility of inorganic salts in a water solution on the basis of the salt effect VLE behavior of methanol in an aqueous solution.[5] The multiple headspace extraction (MHE) GC method is based on the repeated extraction of an equilibrated headspace from a sample vial; both the partition coefficient and VOC solute concentration in the initial aqueous sample can be calculated through MHE GC measurements.[4] The concept of this study was to place a well-mixed aqueous solution with an excess amount of an organic solute of interest in a closed headspace sample vial and to then perform MHE (with the replacement of the extracted vapor with inert gas) to gradually remove the excess solute from the vial. Because the equilibrium vapor concentration decreases dramatically when there is no excess amount of solute remaining in the solution system, the solute saturation point, that is, its solubility, in water could be determined by the observation of the vapor concentration change (by GC) after each headspace extraction.

In this article, we demonstrate a novel MHE GC method for the determination of monomer solubility in water. This method is very simple and automated and can easily be applied to the investigation of solubility at elevated temperatures.

EXPERIMENTAL

Chemicals

Analytical-grade methyl methacrylate (MMA) and styrene were obtained from Fisher (Pittsburgh, PA). A methanol (800 ppm) water solution was prepared for a sample-size-related headspace equilibration study. Deionized water was used in the standard and sample solution preparation.

Apparatus and operation

All measurements were carried out with an HP-7694 automatic headspace sampler and model HP-6890 capillary gas chromatograph (Agilent Technologies, Palo Alto, CA).

For GC, we used a HP-5 capillary column with a film size of 30 m $\times$ 0.35 mm $\times$ 0.25 μm. The column operating temperature was 30°C; the carrier gas helium flow was 3.8 mL/min. A flame ionization detector was used with hydrogen and air flows of 35 and 400 mL/min, respectively. Headspace operating conditions were 5 min of strong shaking for the equilibration of the sample at the desired temperature, a vial pressurization time of 0.2 min, a sample loop fill time of 1.0 min, and a loop equilibration time of 0.05 min. The headspace sample was repeatedly withdrawn from the sample vial in a cycle time of 12 min. To avoid a very large flame ionization detector signal, a GC splitting injection mode or with a headspace sampling loop with a small volume was necessary. With these GC conditions, many monomer compounds with lower molecular weights give a chromatographic retention time less than 10 min. The retention time for MMA measurement in this study was about 2.2 min.

For each analysis, an excess amount of organic solvent was added into a headspace sample vial containing a given volume of water. After the organic solvent and water were mixed by strong hand shaking or ultrasonic agitation, the closed sample was placed in the headspace sampler tray for further equilibration at the desired temperature, MHEs, and GC measurements.

Calibration was conducted with the same MHE GC measurement procedure with a standard solute–water solution in which the concentration of solute was known. The standard solution was prepared by the accurate addition of a desired amount of pure organic monomer into 20 mL of water, and then the closed vial was strongly shaken to aid equilibration.

In this work, 2-mL solutions were used in all of the MHE GC measurements.

RESULTS AND DISCUSSIONS

Sample preparation

A sample aqueous solution with an excess of monomer can be simply made by the addition of a certain volume of pure organic solvent (monomer) into a given volume of water. For a monomer with a specific gravity lower than that of water, the added solvent will form a separate phase on the surface of the aqueous solution; otherwise, it will form a separate phase at the bottom of the vial. Because of the hydrophobicity of most monomers, the interfacial area between the two liquid phases is relatively small. Therefore, it will take a very long time to achieve a saturated solute concentration in the aqueous phase. In this study, we equilibrated the two liquid phases by very strong hand shaking. A suspension of monomer droplets in water resulted after such shaking. The further equilibration of the two liquid phases was conducted automatically with the strong vial shaking mode in the headspace sampler at the studied temperature. The separate phase on the surface of the aqueous solution formed again during the equilibration, especially for monomers with low specific gravities (e.g., styrene) and at a higher temperature. However, this could be

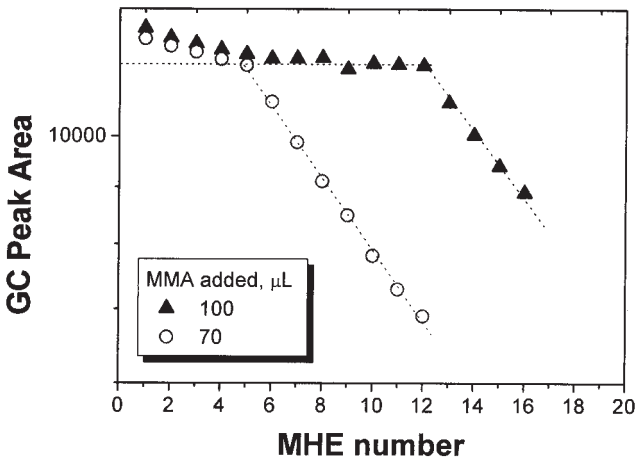

Figure 1 Vapour concentration changes during MHE on MMA aqueous solution samples at 60°C.

overcome by the addition of a very small amount (10 ppm) of surfactant. The test showed that the presence of a small amount of surfactant did not affect the solute vapor–liquid equilibrium, which agreed with results reported by Anderson.[6]

Removal of the excess solute by MHE

After some time, VLE in the sample vial was achieved. By each MHE, a part of the vapor was vented from the vial and was replaced with inert gas. As a result, re-equilibrations in the vapor–liquid and liquid–liquid phases took place. During the re-equilibration process, the solute in the aqueous phase exerted a vapor phase, and the monomer in organic droplets dissolved into the aqueous phase. Thus, the excess monomer in the sample vial was eventually depleted after a number of headspace extractions. Because a separate monomer phase exerted its full vapor pressure, the vapor solute concentration in each headspace measurement held constant as long as a separate monomer phase remained.

Figure 1 shows the results from the MHE GC measurements on two samples with different amounts of MMA added to 2 mL of water at a temperature of 60°C. As shown, the vapor concentration decreased slightly in the initial headspace extractions and then dropped significantly at the 5th and 12th headspace extractions, respectively, for the two experiments. After several headspace extractions, the vapor concentration signal tended to a constant reading. It was also obvious that when more MMA was added, more headspace extractions were needed to vent the excess monomer (above its solubility in water) out of the vial. The transition points in these two experiments corresponded to the solubility limit in these solutions. As shown in Figure 1, although different amounts of MMA were added, the vapor solute concentrations in these two experiments were the same, which corresponded to the solubility of the solute in the aqueous phase.

MHE GC method for VLE study

As also shown in Figure 1, a linear relationship between the logarithmic GC peak area and headspace extraction number was obtained after the transition point, which indicated the absence of a monomer liquid phase. This could be described by the mathematical equations derived in our previous work.[4]

In MHE GC measurement, a part of the solute mass in the vapor ($m_{EX,solute}$) is vented out of the sample vial through each headspace extraction; this can be expressed as a certain fraction of the solute vapor in the headspace before venting:

$$m_{EX,solute} = \varphi C_G V_G \tag{1}$$

where ϕ is volumetric flow fraction for each extraction, C_G is the vapor solute concentration, and V_G is the headspace volume.

After a number of headspace extractions, the mass remaining in the vial (m_n) can be written as

$$m_n = (C_{Gn}V_G + C_{Ln}V_L) = m_1 - V_G(\varphi_1 C_{G1} + \varphi_2 C_{G2} + \cdots + \varphi_{n-1} C_{G(n-1)}) = m_1 - V_G \sum_1^{n-1} \varphi_i C_{Gi} \tag{2}$$

where C_{Ln} and V_L represent the solute concentration in liquid phase at n^{th} headspace extraction and liquid phase volume, respectively.

The sample volumetric flow fractions are constant, that is, $\phi_1 = \phi_2 = \ldots = \phi_i = \phi_{n-1} = \phi$, although the absolute solute mass extracted out is reduced because of the reduced monomer concentrations in the liquid and vapor phases within the vial.

For infinitely dilute solutions, that is, when the concentration of the solute is very low, the molecular solute-to-solute interactions in the aqueous phase can be neglected. Thus, the dimensionless Henry's constant (H_c) can be expressed as follows:

$$H_c = \frac{C_{G1}}{C_{L1}} = \frac{C_{G2}}{C_{L2}} = \frac{C_{G3}}{C_{L3}} = \cdots = \frac{C_{Gn}}{C_{Ln}} \tag{3}$$

If eq. (3) is substituted into eq. (2), we have

$$C_{Gn}\left(V_G + \frac{V_L}{H_c}\right) = m_1 - \varphi V_G \sum_1^{n-1} C_{Gi} \tag{4}$$

Thus, we can finally obtain eq. (5) by reorganizing eq. (4) as follows:

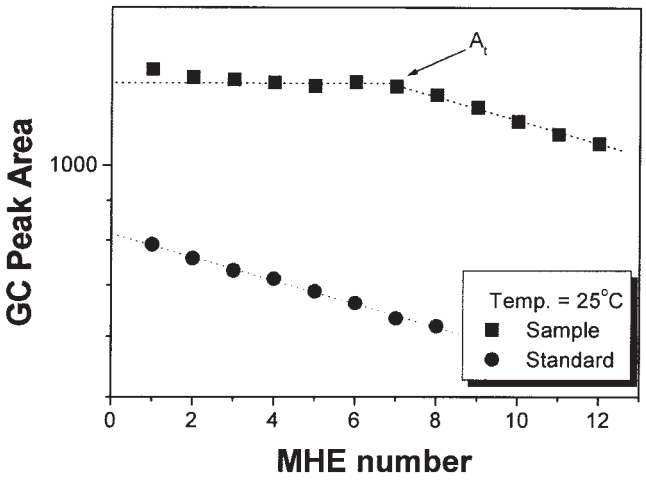

Figure 2 Comparison of vapour concentration changes in standard MMA solution and a sample solution with an excess amount of MMA, at a temperature of 25°C.

$$\sum_{1}^{n-1} A_i = a + bA_n \tag{5}$$

where $i = 1, 2, \ldots, n \geq 2$, and A is the GC signal peak area at ith headspace extraction, which is proportional to the vapor concentration of solute, that is, $A = fC_G$, where f is a calibration constant with

$$a = \frac{fm_1}{\varphi V_G} \tag{6}$$

and

$$b = -\frac{1}{\varphi}\left(1 + \frac{1}{H_c} \times \frac{V_L}{V_G}\right) \tag{7}$$

where m_1 is the initial solute mass and the constants a and b can be obtained from linear regression.

Equation (5) for MHE GC application is only valid for the headspace measurements after the transition point. Therefore, at the same temperature, the slope b in Figure 2 is identical to those in Figure 1, although the amounts of MMA added in the solutions were totally different (i.e., their VLE partitioning in these solutions were the same). The solubility of MMA could be calculated according to the GC peak areas at the transition point in Figure 1 through a calibration based on a standard MMA solution.

Solubility determination and method calibration

Figure 2 shows MHE GC measurements on a MMA standard solution (1.00%) and a sample solution with an excess amount of MMA, respectively, at a temperature of25°C. The GC peak area at the transition point (A_t) corresponded to the solubility of the solute. The method calibration was conducted based on a standard monomer–water solution whose solute concentration was known.

As described previously, by plotting the summed GC peak area ($\sum_{1}^{n-1} A_i$, versus the GC peak area at each headspace extraction under VLE and conducting a linear regression, we obtained the intercept and slope (a_1 and b_1, respectively) from eq. (8) for the standard solution and a_s and b_s from eq. (9) from the sample solution:

$$y = a_1 + b_1 x \tag{8}$$

and

$$y = a_s + b_s x \tag{9}$$

They are shown in Figure 3. In theory, the slopes of the curves for both the standard and sample MHE GC measurements should be the same, that is, $b_1 = b_s$. Our experimental results in Figure 3 also show that the slopes from the two separate experiments were identical.

According to eq. (6), the initial solute concentration (C_1) in the standard solution and the saturated concentration (C_s) in the sample can be written as

$$C_1 = \frac{m_1}{V_L} = \frac{a_1 \varphi V_G}{f V_L} \tag{10}$$

and

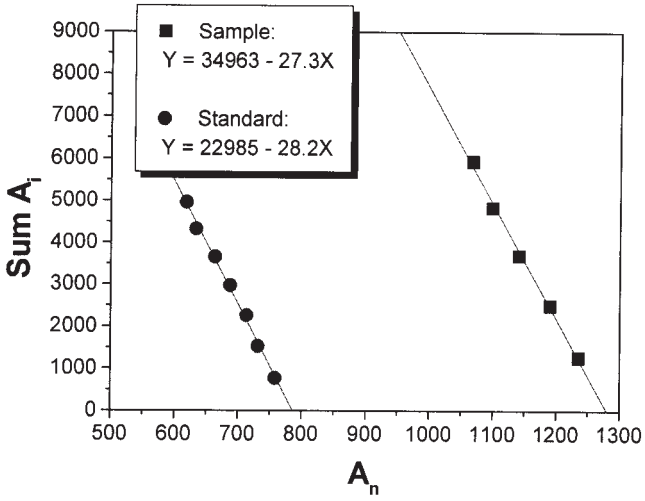

Figure 3 The relationships between plotting summed GC peak area, $\Sigma_1^{n-1} A_i$, vs. the GC peak area at each headspace extraction under VLE and conducting for both sample and standard MMA solutions (the original GC peak area data were from that in Fig. 2).

$$C_s = \frac{m_s}{V_L} = \frac{a_s \varphi V_G}{f V_L} \tag{11}$$

Thus, the solubility of the monomer in the solution can be calculated as

$$C_s = \frac{a_s}{a_1} C_1 \tag{12}$$

The solubility of the solute can be also determined by substituting A_t and A_{t+1} (the GC peak area at point next to the transition point) from the sample measurement in eq. (5):

$$A_t = a_s + b_1 A_{t+1} \tag{13}$$

to obtain the a_s value. Because a_1 and b_1 can be obtained on the basis of the MHE GC measurements on a standard solution, the solubility can be calculated by the follows:

$$C_s = \frac{A_t - b_1 A_{t+1}}{a_1} C_1 \tag{14}$$

Method precision and validation

In a previous work,[4] we presented a detailed mathematical precision analysis for the MHE GC method application in a VLE study. As shown in Figure 1 of ref. 4, a good measurement precision in solute concentration determination was obtained if the volume ratio of vapor to liquid was greater than 7, in which case, a relative standard deviation within 5% was achieved.

To verify the method in this study, we applied this MHE GC method to determine the solubilities in MMA and the styrene aqueous solution at a temperature of 25°C, (at which temperature their solubility data were available[7]). The MMA solubility data obtained from this method were based on the two sets of experimental data obtained from the sample and standard solution measurements, which are illustrated in Figures 2 and 3. A comparison of the results for these two monomers obtained by this method and the methods used in the references are listed in Table I. The results were very close, indicating that the results from this method were justifiable.

TABLE I
Comparison of solubility of MMA and styrene in aqueous solutions at 25°C measured by the present method and those from literature [7].

Organics	Present Method (wt %)	Literature Data (wt%)	Difference (wt%)
MMA	1.52	1.56	0.04
Styrene	0.034	0.032	0.002

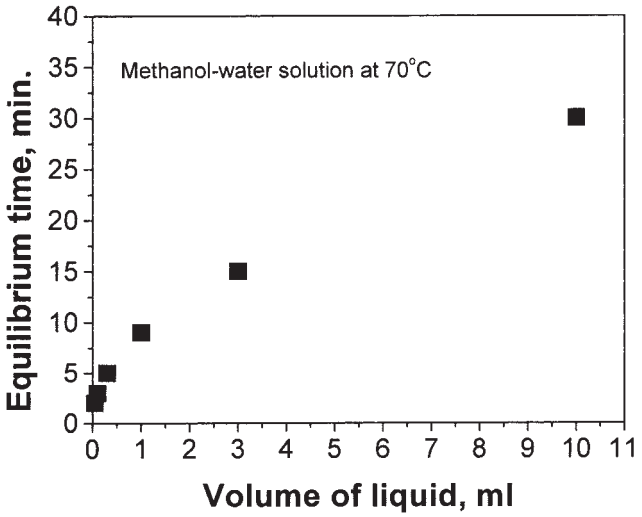

Figure 4 Sample size effect on vapour-liquid phase equilibration time.

This method is suitable for application to aqueous solutions where the solubilities of the organic solutes are very low because the VLE partitioning behavior will no longer agree with the Henry's law if the organic solute has a very large solubility. However, it is the very low end of monomer water solubility that is so difficult to measure by conventional methods.

Sample size and equilibration time

In this study, the total volume ($V_T = V_G + V_L$) of the headspace sample vial was about 20 mL. As mentioned previously, a good measurement precision requirement could be achieved when the volume ratio of vapor to liquid was larger than 7.[4] Thus, the liquid sample volume needs to be smaller than 2.5 mL. In this work, a sample volume of 2 mL was used for all of the experiments.

In a previous work,[8] it was reported that VLE time is independent on the solute species at a given temperature. Unlike monomer compounds, methanol can completely dissolve in water and has a lower volatility in aqueous solution. Therefore, a methanol aqueous solution could be easily prepared, stored, and sampled in the experiment. In this work, we used a methanol aqueous solution to investigate the sample size effect on VLE time. Detailed procedures for the VLE time determination were described in ref. 8. As shown in Figure 4, VLE was a function of time. A quicker VLE was achieved with a smaller sample size. Therefore, the information in Figure 4 was a good reference for choosing a proper equilibration time in the experiment. In this study, headspace in the vial was withdrawn at a time interval of 12 min, in which the VLE was basically achieved according to Figure 4. Also, temperature had a minor effect on the VLE. A higher temperature facilitated the solute equilibration parti-

tioned between the two phases. A completely static VLE was not necessary because every MHE procedure in the headspace sampler was precisely repeated. Thus, we could conduct the measurement with a short equilibration time on the basis of a prestatic time to make the experiment more efficient.

CONCLUSIONS

We developed an MHE GC technique for the determination of monomer solubility in an aqueous solutions. The method is very simple and automated and can be easily used for organic solute solubility measurement at elevated temperatures. The measured solubilities for MMA and styrene by this method matched the data reported in the literature.

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