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Sample Preparation

Estimation of effective diffusion coefficients for benzene and toluene in PDMS for direct solid phase microextraction

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ABSTRACT

Polydimethylsiloxane (PDMS) is commonly used as the coated polymer in the solid phase microextraction (SPME) technique. Based on the principle of partitioning, PDMS/SPME can be a fast, economic and solvent-free sampling method to extract volatile organic compounds (VOCs) from gaseous or aqueous samples. This study experimentally investigated the adsorption of benzene and toluene onto PDMS/SPME, and estimated the effective diffusion coefficients of benzene and toluene in the PDMS coating. The results showed that the effective diffusion coefficients of these two compounds did not change with the concentrations of the gaseous or aqueous samples. The effective diffusion coefficients were found to linearly increase with the stirring speeds of the aqueous solution. The empirical model proposed in this study can be used to estimate the effective diffusion coefficients and extraction time at different stirring speeds, which will contribute to the practical applications of the SPME technique.

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1. Introduction

Solid phase microextraction (SPME) is a solvent-free sample preparation technique. As shown in Fig. 1, polymeric materials, such as polydimethylsiloxane (PDMS) and polyacrylate (PA), are coated onto the outer layer of the fused silica rod of the SPME device. According to the principle of partitioning, the analyte is adsorbed from the sample matrix onto the coating stationary phase. The concentrated extract is then transferred to an instrument, such as a gas chromatograph, for thermal desorption and analysis. The SPME technique can simplify the four steps of sampling, extraction, condensation and introduction of the sample into the analytical instrument, while reducing sample loss due to the extraction steps. In comparison to the traditional solid phase extraction methods, SPME is fast, easy to use, and has lower detection limits [1].

Prior to using the SPME technique for sampling and analysis, the first step is to select the appropriate polymer

as the SPME coated material to adsorb the analyte, followed by determining the equilibrium extraction time for SPME. In the direct SPME method, the polymeric coating is directly exposed to the sample matrix for extraction. Since the polymeric coating is very thin (7–100 μm), rapid extraction can be realized. For the gaseous sample, sorption equilibrium can be rapidly reached due to the relatively higher diffusion coefficient of analytes in the gas.

For the aqueous sample, the analyte is transferred by diffusion through the bulk solution and then into the coated polymer, which requires a longer equilibrium time as compared to the gaseous sample [2,3]. Under ideal agitation conditions, the effect of diffusion of analytes in the bulk solution can be negligible. The time to reach adsorption equilibrium is essentially determined by the diffusion of analytes in the coated polymer of the SPME device. Eq. (1) can be used to estimate the equilibrium time t_{eq} to extract the analyte from the aqueous sample [3–5].

$$t_{eq} = \frac{L^2}{2D_f} \quad (1)$$

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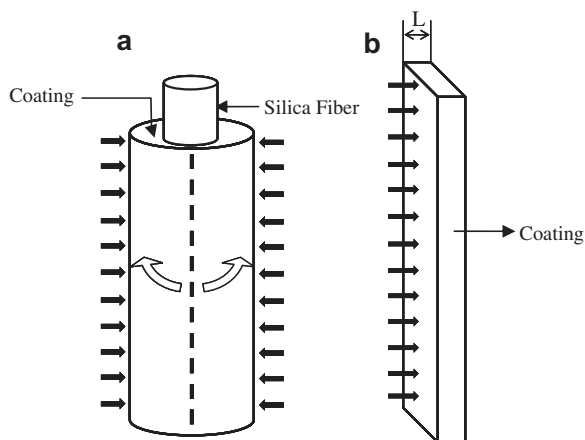


Fig. 1. Configuration of PDMS fiber coated on the fused silica rod for a SPME device.

where, L is the thickness of the SPME coating; D_f is the diffusion coefficient (L^2T^{-1}) of the analyte in the SPME coating.

D_f should be determined first when using Eq. (1) to estimate the extraction time for SPME. However, there is little research on the values of D_f for SPME. Generally, the extraction time for SPME is experimentally determined using a trial and error method. In this study, individual batch adsorption experiments were conducted to obtain the adsorption curves for benzene and toluene using SPME. Based on Fick's law, the diffusion coefficients of benzene and toluene in PDMS/SPME were determined for gaseous and aqueous samples. The effects of the sample concentration and the stirring speed on the diffusion coefficients are discussed. The results of this study can be used to determine the equilibrium time for direct extraction using SPME, and facilitate the application of polymers in the SPME technique.

2. Experimental

2.1. Materials

The SPME device was purchased from Supelco Co (Bellefonte, PA). A PDMS membrane with a thickness of $100\ \mu\text{m}$ was used as the SPME coating. Because the polarity of PDMS is low, non-polar benzene and toluene were selected as the target extracts. Benzene (Merck, Darmstadt, Germany) and toluene (Mallinckrodt Baker, Phillipsburg, NJ) were of ACS grade with purity greater than 99%.

2.2. Experiments for gaseous samples

The standard solutions were prepared by dissolving different volumes of benzene and toluene individually in a 5 mL glass vial filled with methanol. The standard solutions were collected using a microlitre syringe and injected directly into 5 mL glass vials sealed with open top caps equipped with Teflon lined septa. Thirty gaseous samples of different concentrations of benzene and toluene were prepared with concentration range of 0.1–35.1 mg/L.

The sample vials were placed in a low temperature incubator (LB-BOD-300, Taiwan) at a temperature of $25 \pm 1\ ^\circ\text{C}$ for 1 h to allow benzene and toluene to volatilize before the extraction experiments. In order to obtain the adsorption curve, the SPME device was put into the sample vials to adsorb benzene or toluene for different periods of time. After the exposure period, the SPME device was then taken out and injected into a gas chromatograph (Auto-System XL, Perkin Elmer, Norwalk, Conn.) equipped with a flame ionization detector (FID). The temperature of the capillary GC column (Equity^{TM-5}, Supelco, Bellefonte, PA) was set at an initial temperature of $100\ ^\circ\text{C}$ for 1 min, and then increased to $180\ ^\circ\text{C}$ at a rate of $20\ ^\circ\text{C}/\text{min}$. The temperatures of the injection port and detector were maintained at $220\ ^\circ\text{C}$ and $250\ ^\circ\text{C}$, respectively.

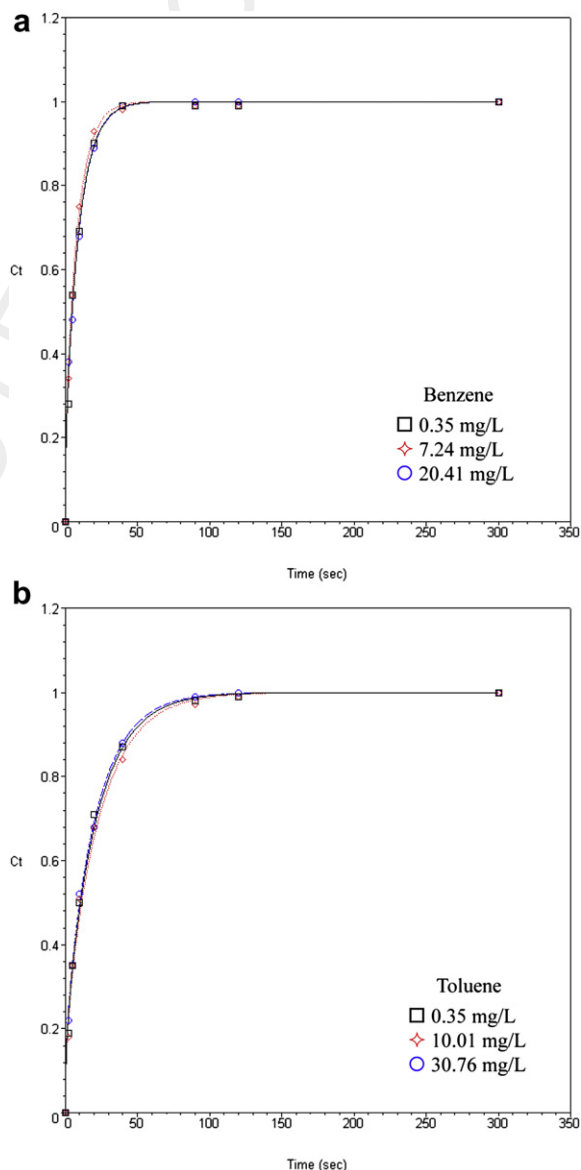


Fig. 2. Adsorption concentrations versus time for gaseous samples.

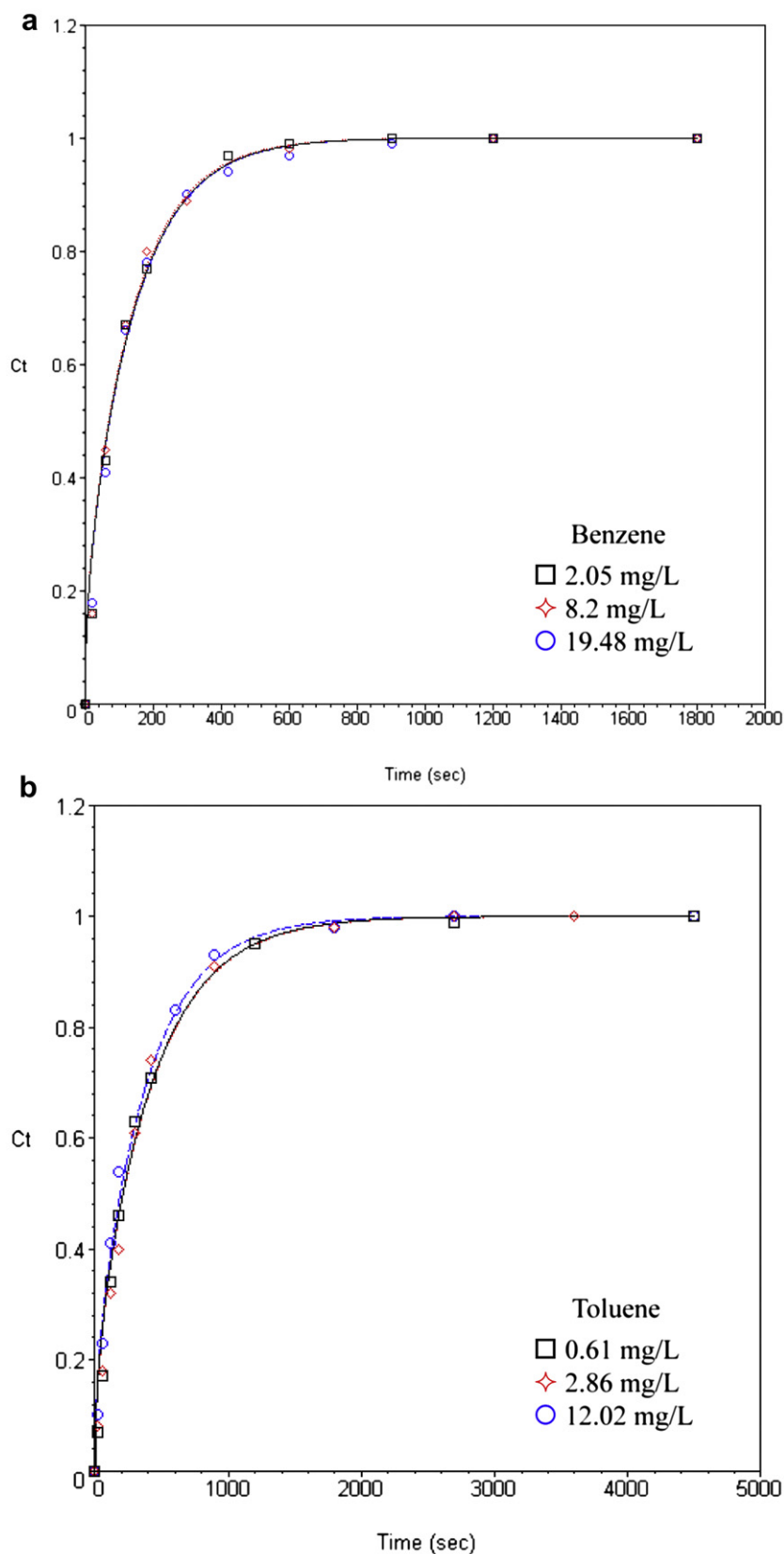


Fig. 3. Adsorption concentrations versus time for aqueous samples stirred at 1150 rpm.

2.3. Experiments for aqueous samples

In this experiment, a 5 mL glass vial with a stirring bar was completely filled with deionized water without headspace. The aqueous solution was prepared by spiking different volumes of neat benzene and toluene, respectively, into the 5 mL vial sealed with an open-top cap. The aqueous concentrations of the 30 samples ranged between 0.08 and 35.85 mg/L. When the agitation speed on the digital display of the magnetic stirrer (PC-410D, Corning, USA) was more than 1250 rpm, there was irregular stirring in the 5 mL sample vial. As a result, the agitation condition for this study was to maintain the maximum stirring speed at 1150 rpm [6].

The aqueous sample and magnetic stirrer were inserted into a low temperature incubator at a temperature of 25 ± 1 °C for the extraction experiment. The sample vial was placed onto the magnetic stirrer at a stirring speed of 1150 rpm. The SPME device was injected separately into the sample vials for different adsorption times. The SPME device was then taken out and exposed in the injector of the GC-FID for 5 min. The oven of the GC was kept at 200 °C, and the temperatures of injector and detector were 220 °C and 250 °C, respectively.

For the experiments with different agitation speeds, aqueous concentrations of benzene and toluene were prepared at concentrations of 0.85 mg/L and 1.01 mg/L, respectively. The aqueous samples were extracted with 30 stirring speeds. The experimental procedures were the same as the aqueous concentration study.

3. Results and discussion

3.1. Estimation of diffusion coefficients

Mass transfer of the organic solvent into the coated polymer of the SPME device can be described by the solution-diffusion model. The organic solvent is first

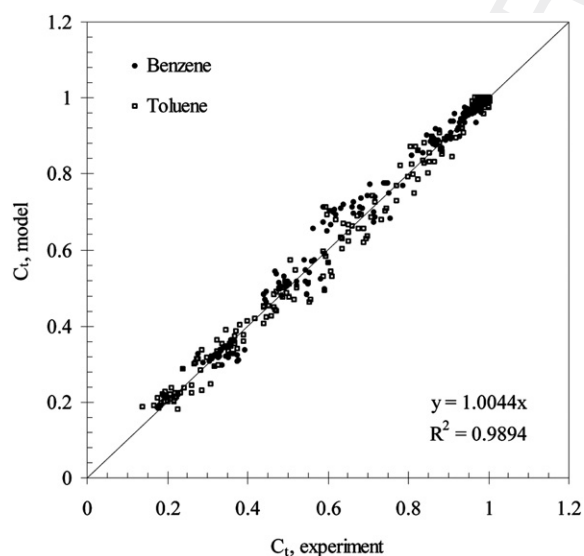


Fig. 4. Comparison of experimental absorption concentrations with modeling results for gaseous samples.

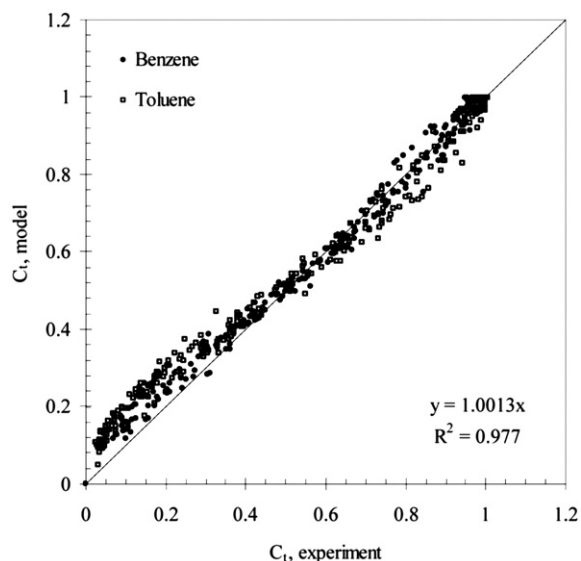


Fig. 5. Comparison of experimental absorption concentrations with modeling results for aqueous samples.

attached onto the surface of the coated polymer and then diffuses into the polymer [7–9]. As shown in Fig. 1, the PDMS membrane is coated on the surface of the silica fiber of the SPME as a hollow cylinder. When the thickness of the PDMS coating L is very thin, it can be considered as a plate. Hence, the diffusion of the organic solvent into the PDMS coating can be expressed by Fick's law with a constant diffusivity as follows:

$$\frac{\partial C_f}{\partial t} = D_f \frac{\partial^2 C_f}{\partial x_f^2} \quad (2)$$

where, C_f is the organic solvent concentration in the PDMS coating (ML^{-3}); and x_f is the distance along the direction of diffusion (L).

Prior to the extraction of the gaseous or aqueous samples, the concentration of the organic solvent in the PDMS membrane is zero. The organic solvent molecules diffuse into the PDMS membrane, but cannot enter into the fused silica rod in the centre. As the concentrations of the

Table 1
Diffusion coefficients of benzene and toluene gaseous samples for PDMS membrane.

Benzene ($10^{-6} \text{ cm}^2/\text{s}$)	Toluene ($10^{-6} \text{ cm}^2/\text{s}$)	Conditions	Reference
2.8		25 °C, Midland Silicones Ltd.	[11]
4.8	4.0	38 °C, Silastic™, Dow Corning	[12]
6.4	5.6	25 °C, Silastic™, Dow Corning	[13]
1.34	1.15	25 °C, Silastic™, Dow Corning	[14]
2.2	1.8	25 °C, Silastic™, Dow Corning	[15]
0.47–0.99	0.18–0.32	25 °C, Shin-Etsu Co.	[16]

organic solvent in the samples are very low, the adsorption of the organic solvent onto the sample vials can be neglected. Therefore, the initial and boundary conditions of Eq. (2) are as follows:

$$C_f = 0 \quad 0 \leq x_f \leq L \quad t = 0$$

$$\frac{\partial C_f}{\partial t} = 0 \quad x_f = L \quad t > 0$$

As the PDMS coating is far smaller than the sample matrix in terms of volume, the organic solvent concentration in PDMS, C_f (ML^{-3}), can be represented as follows:

$$\frac{C_f}{C_\infty} = 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \exp \left[-D_f(2n+1)^2 \pi^2 \frac{t}{L^2} \right] \cos \frac{(2n+1)\pi x_f}{L} \quad (3)$$

where, C_∞ is the organic solvent concentration in the PDMS coating when the adsorption reaches equilibrium (ML^{-3}).

From Eq. (3), the mass of the organic solvent adsorbed in the PDMS coating, M_t (M), can be written as follows:

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp \left[-D(2n+1)^2 \pi^2 \frac{t}{L^2} \right] \quad (4)$$

where, M_∞ is the mass of the organic solvent adsorbed in PDMS at equilibrium.

In this study, the mass of the organic solvent adsorbed by PDMS/SPME was quantified by GC/FID. Therefore, the relative adsorption concentration of organic solvents in the PDMS coating C_t can be determined by the following equation:

$$C_t = \frac{M_t}{M_\infty} = \frac{A_t}{A_\infty} \quad (5)$$

where, A_t and A_∞ are the GC/FID peak area for PDMS/SPME sampling at time t and at equilibrium, respectively.

The sorption curve of the organic solvent in PDMS was determined by plotting C_t against $(\text{Time})^{0.5}$. According to Eq. (4), the diffusion coefficient of the solvent in the PDMS coating can be determined by the sorption curve and the following equation [10]:

$$D_f = \pi \left(\frac{L\theta}{4} \right)^2 \quad (6)$$

where, θ is the slope of the initial linear line of the sorption curve (before equilibrium at 50–55%).

Figs. 2 and 3 illustrate the experimental adsorption results of benzene and toluene for the gaseous and aqueous samples, respectively. For the gaseous and aqueous samples of different concentrations, the equilibrium time of PDMS/SPME extraction did not change significantly. Using the sorption curve, the diffusion coefficients of benzene and toluene in the PDMS coating were determined by Eq. (6). The adsorption concentrations of benzene and toluene in PDMS/SPME were further obtained by substituting D_f into Eq. (4). As shown in Figs. 2 and 3, D_f obtained by Eq. (6) can be used to simulate well the experimental adsorption results of the gaseous and

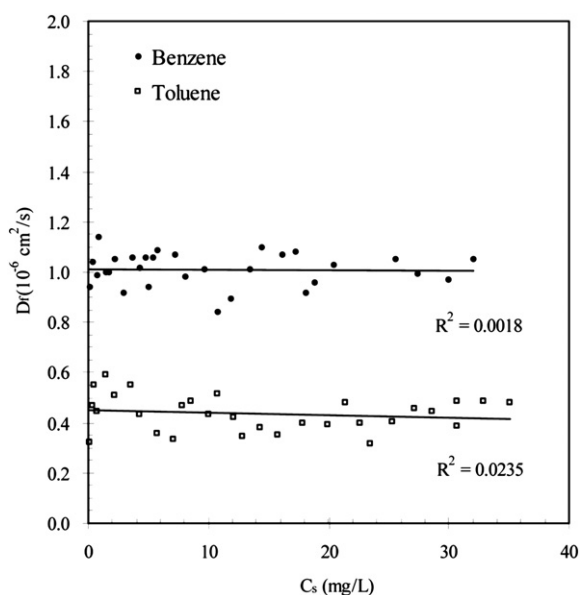


Fig. 6. Diffusion coefficients of benzene and toluene in PDMS/SPME for gaseous samples.

aqueous samples. Figs. 4 and 5 present the comparison of experimental C_t values with C_t determined from Eqs. (4) and (6) for the gaseous and aqueous samples, respectively. As indicated in Figs. 4 and 5, the slopes of the regressions were 1.0044 and 1.0013, respectively, indicating good correlation ($R^2 \geq 0.977$). Therefore, Eq. (6) can be used to estimate the diffusion coefficient of benzene and toluene in PDMS/SPME for either gaseous or aqueous samples.

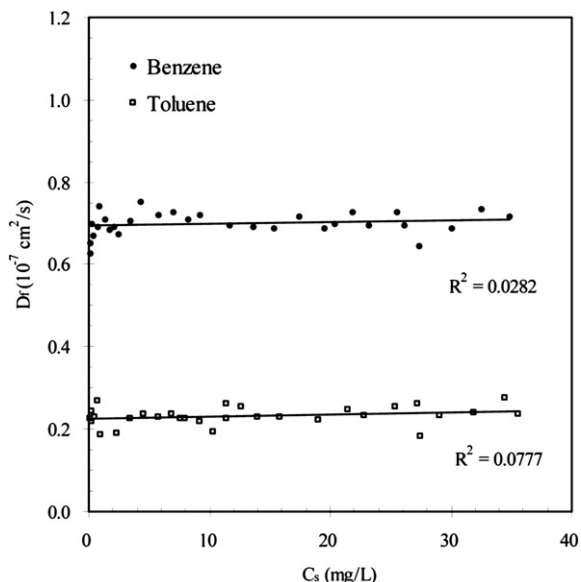


Fig. 7. Diffusion coefficients of benzene and toluene in PDMS/SPME for aqueous samples.

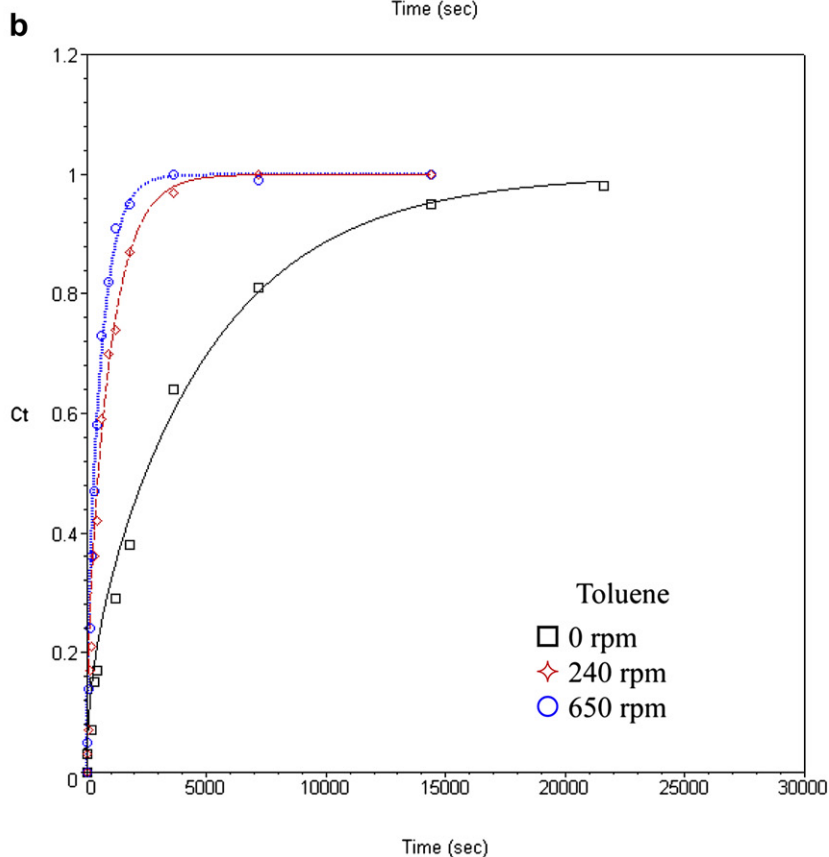
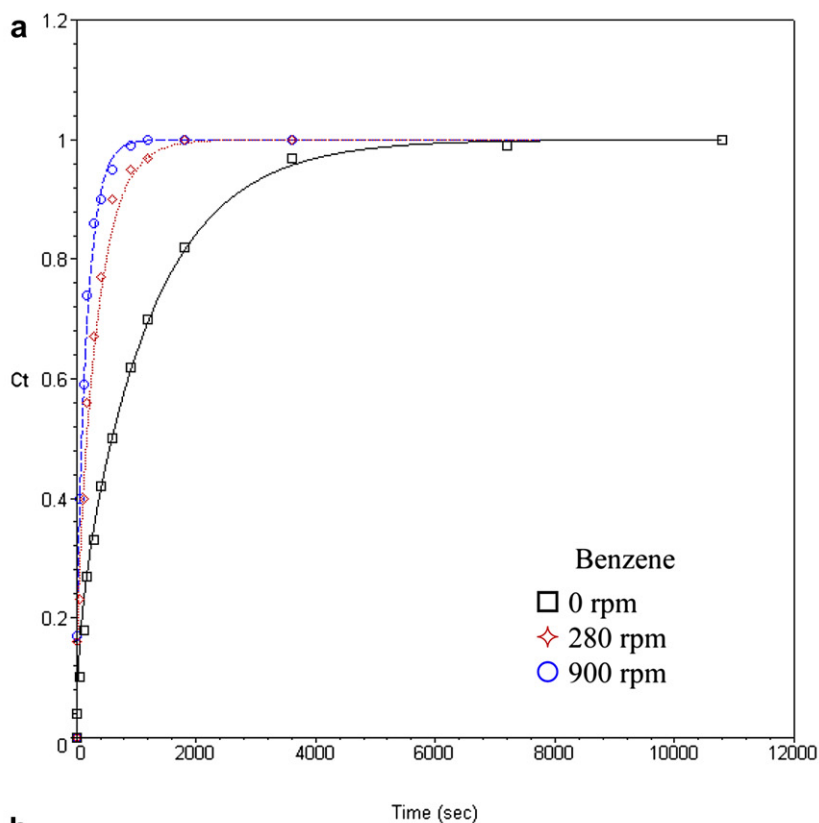


Fig. 8. Adsorption concentrations versus time for aqueous samples stirred at different speeds.

3.2. Effect of sample matrix

For the gaseous samples, the diffusion coefficients of benzene and toluene in PDMS/SPME obtained using Eq. (6) were 1.01 ± 0.07 and 0.44 ± 0.06 (10^{-6} cm²/s), respectively. As shown in Table 1, several researchers [11–16] have indicated that the range of the diffusion coefficients of benzene and toluene gas in PDMS are 0.47–6.4 and 0.18–5.6 (10^{-6} cm²/s), respectively. The diffusion coefficients estimated herein were consistent with the previous studies. However, there is no literature data on the PDMS/SPME experiments.

The diffusion coefficients of benzene and toluene aqueous solutions in PDMS/SPME were 0.7 ± 0.03 and 0.23 ± 0.02 (10^{-7} cm²/s), respectively, which were approximately 10 times smaller than the diffusion coefficients of the gaseous samples. This may be explained by the effect of benzene and toluene hydrate in the aqueous solution [17]. The molecular size of benzene hydrate is larger, resulting in a lower diffusion coefficient. On the other hand, the clustering of water molecules on the surface of PDMS/SPME may reduce the mobility of benzene and toluene molecules.

Figs. 6 and 7 show the diffusion coefficients of benzene and toluene in PDMS/SPME for different sample concentrations. The correlations between the diffusion coefficients and the sample concentrations were $R^2 \leq 0.0777$, suggesting that diffusion coefficients would not change with the concentrations of either gaseous or aqueous samples.

By substituting D_j into Eq. (1) to estimate t_{eq} , it was found that the equilibrium time of benzene and toluene gaseous samples was 48.7 ± 5.2 and 117.2 ± 13.2 s, respectively. From the adsorption experiments, the equilibrium time was 50.3 ± 5.7 and 120.8 ± 14.1 s for benzene and toluene gas, respectively. According to the statistical analysis of the t -test, the equilibrium time obtained by Eq. (1) and the adsorption experiments was not significantly different ($p > 0.05$) for gaseous samples.

Martos and Pawliszyn [18] investigated the dynamic sampling of toluene gas using SPME with PDMS coating (100 μ m, Supelco, Canada). In that study, toluene gas of a constant concentration uniformly passed through the SPME device, which differed from the static sampling of this study. Martos and Pawliszyn indicated that the equilibrium time of PDMS/SPME to adsorb toluene gas was 60 s which was approximately half t_{eq} of this study. Previous researchers [2,19] also pointed out that the equilibrium time obtained by dynamic sampling would be shorter than that by static sampling. For dynamic sampling, the analyte is continuously delivered to the PDMS coating, and the effect of analyte diffusion in air would be minimized.

3.3. Effect of agitation condition

Fig. 8 presents the experimental adsorption results of benzene and toluene at different stirring speeds. Without stirring the aqueous solution, the equilibrium times for benzene and toluene adsorption onto PDMS/SPME were approximately 105 and 430 min, respectively. As the stirring speed increased, t_{eq} was shortened and the slopes of the initial stage of adsorption profile, shown in Fig. 8, were increased. Consequently, the diffusion coefficients of

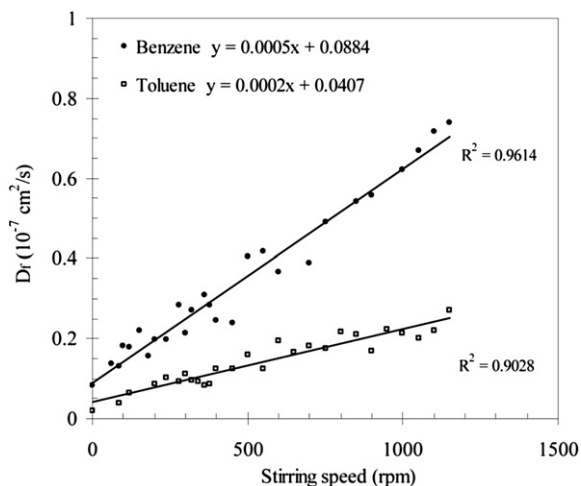


Fig. 9. Correlations of diffusion coefficients to stirring speed for aqueous samples.

benzene and toluene in PDMS/SPME increased with the stirring speed. When PDMS/SPME was immersed in the aqueous solution, there would be a boundary layer around the PDMS coating. The solvent molecules in the bulk solution away from the PDMS–water interface would diffuse to the PDMS–water interface due to a concentration gradient. As the aqueous solution was well mixed, the boundary layer around PDMS/SPME would be thinner. Thus, the equilibrium time for solvent molecules adsorption onto the PDMS coating would be shortened [6].

The effect of agitating condition for aqueous solutions was not taken into account in Eq. (4). As shown in Fig. 8, the diffusion coefficients estimated by Eq. (6) can appropriately simulate the adsorption results of aqueous solutions using Eq.

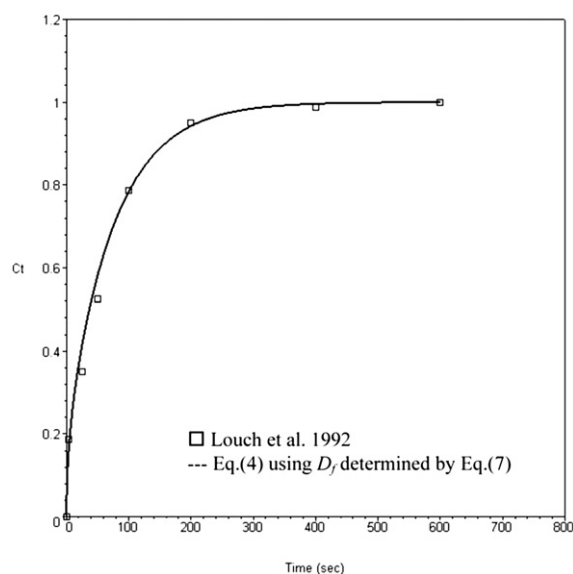


Fig. 10. Concentration profile of simulation and experimental results from literature.

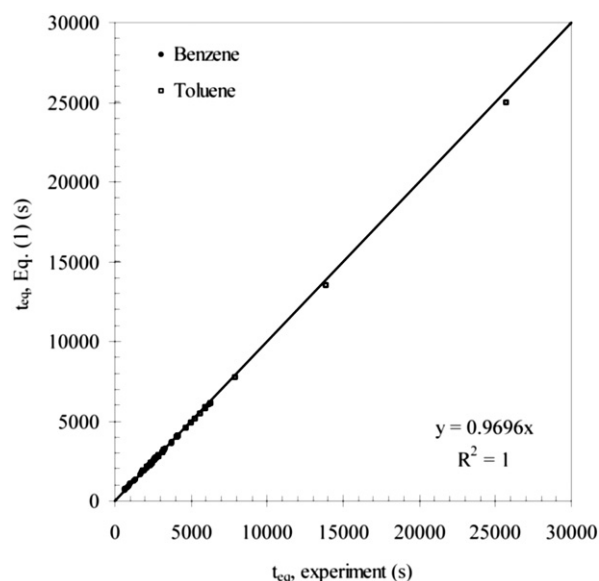


Fig. 11. Comparison of experimental SPME equilibrium time with modeling results for aqueous samples at different agitation conditions.

(4) in the case of different stirring speeds. Therefore, D_f obtained in this study can be characterized as the effective diffusion coefficient of organic solvents in PDMS/SPME. For either benzene or toluene, Fig. 9 shows that D_f was linearly increased with the stirring speeds of aqueous solution. Eqs. (7) and (8) illustrate the correlations between D_f (10^{-7} cm²/s) and the stirring speeds for benzene and toluene aqueous solutions, respectively.

$$D_f = 0.0005 \text{ rpm} + 0.0884 \quad (7)$$

$$D_f = 0.0002 \text{ rpm} + 0.0407 \quad (8)$$

Louch et al. [3] used a SPME device, coated with 97 μm PDMS, to extract benzene from the aqueous solution in a 1.8 mL vial. Fig. 10 indicates the adsorption profile in the case of a magnetic stirring speed of 2500 rpm. The thickness of the PDMS coating and the sample vial were similar to those of this study. By Eq. (7), D_f was calculated to be 1.34 (10^{-7} cm²/s) for 2500 rpm, which could be used to appropriately simulate the experimental results of Louch et al. [3], as shown in Fig. 10. Eqs. (7) and (8), however, can be the empirical models to estimate the effective diffusion coefficient of PDMS/SPME for benzene and toluene aqueous solution agitated at different stirring speeds.

Using Eq. (1), Pawliszyn [4] predicted that the equilibrium time for the benzene aqueous solution adsorbed onto 100 μm PDMS/SPME was approximately 20 s under ideal agitation conditions. In Pawliszyn's study, D_f was equal to 2.8 (10^{-6} cm²/s) which was the diffusion coefficient of benzene gas in PDMS [20]. As shown in Fig. 3, t_{eq} for benzene aqueous solution was approximately 700 s for a stirring speed of 150 rpm. As $D_f = 2.8$ (10^{-6} cm²/s), the estimated stirring speed using Eq. (7) would be as high as 55,800 rpm which, however, cannot be conducted in practice.

For the aqueous samples, Fig. 11 compares the experimental t_{eq} with those determined by Eq. (1) into which D_f obtained using Eq. (6) was substituted. As shown in Fig. 11, they had good agreement ($R^2 = 1$), and there was no significant difference with a statistical analysis of the t -test ($p = 0.88$). Therefore, the effective diffusion coefficient obtained from the model of this study can be employed to estimate the equilibrium time of PDMS/SPME to extract the analyte from gaseous and aqueous samples.

4. Conclusions

In this study, batch experiments were conducted to investigate the adsorption kinetics of organic solvents in PDMS/SPME. Based on Fick's law, the adsorption profiles of PDMS/SPME could be simulated for gaseous and aqueous samples, even in the case of different stirring speeds. Furthermore, the equilibrium time of PDMS/SPME to extract the analyte from gaseous and aqueous samples could be determined using the effective diffusion coefficient. The results showed that the effective diffusion coefficients of benzene and toluene aqueous solution in PDMS/SPME were about 10 times smaller than that of gaseous samples. As a result, the extraction time of SPME in the aqueous solution will be underestimated using the diffusion coefficient obtained from the gaseous sample. For the wide range of sample concentrations, this study found that the effective diffusion coefficients did not change with the concentrations of benzene and toluene. However, the effective diffusion coefficients linearly increased with the magnetic stirring speeds of the aqueous solutions.

Acknowledgments

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References

- [1] J. Pawliszyn, Applications of Solid Phase Microextraction. RSC, Cornwall, UK, 1999.
- [2] Z. Zhang, J. Pawliszyn, Anal. Chem. 65 (1993) 1843–1852.
- [3] D. Louch, S. Motlagh, J. Pawliszyn, Anal. Chem. 64 (1992) 1187–1199.
- [4] J. Pawliszyn, Solid Phase Microextraction - Theory and Practice. Wiley-VCH, New York, 1997.
- [5] H. Lord, J. Pawliszyn, J. Chromatogr. A 885 (2000) 153–193.
- [6] K. Sukola, J. Koziel, F. Augusto, J. Pawliszyn, Anal. Chem. 73 (2001) 13–18.
- [7] Y.Z. Luo, M. Adams, J. Pawliszyn, Anal. Chem. 70 (1998) 248–254.
- [8] X. Liu, J. Pawliszyn, J. Membr. Sci. 268 (2006) 65–73.
- [9] C. Basheer, H.K. Lee, J.P. Obbard, J. Chromatogr. A 968 (2002) 191–199.
- [10] J. Crank, The Mathematics of Diffusion. Oxford, New York, 1975.
- [11] A.C. Newns, G.S. Park, J. Polymer. Sci. 22 (1969) 927–937.
- [12] A.A. Sysoev, R.A. Ketola, I. Mattila, V. Tarkkainen, T. Kotiaho, Mass Spectrom. 212 (2001) 205–217.
- [13] M. Alenander, E. Boscaini, W. Lindinger, T.D. Mark, Mass Spectrom. 223–224 (2003) 763–770.
- [14] E. Boscaini, M.L. Alexander, P. Prazeller, T.D. Märk, Int. J. Mass Spectrom. 239 (2004) 179–186.
- [15] K.S. Oh, Y.M. Koo, K.W. Jung, Int. J. Mass Spectrom. 253 (2006) 65–70.
- [16] S.J. Lue, S.F. Wang, L.D. Wang, W.W. Chen, K.M. Du, S.Y. Wu, Desalination 233 (2008) 277–285.
- [17] S. Mishima, T. Nakagawa, J. Appl. Polym. Sci. 78 (2000) 1304–1311.
- [18] P.A. Martos, J. Pawliszyn, Analytica Chim. Acta 69 (1997) 206–215.
- [19] M. Chai, J. Pawliszyn, Environ. Sci. Technol. 29 (1995) 693–701.