**Polymer-water partition coefficients in polymeric passive samplers**

Abstract

Passive samplers are of the most applied methods and tools for measuring concentration of hydrophobic organic compounds in water (***c1W***) in which the polymer-water partition coefficients (*D*) are of fundamental importance for reliability of measurements. Due to the cost and time associated with the experimental researches, development of a predictive method for estimation and evaluation of performance of polymeric passive samplers for various hydrophobic organic compounds is highly needed and valuable. For this purpose, in this work, following the fundamental chemical thermodynamic equations governing the concerned local equilibrium, successful attempts were made to establish a theoretical model of polymer-water partition coefficients. Flory–Huggins model based on the Hansen solubility parameters was used for calculation of activity coefficients. The method was examined for reliability of calculations using collected data of three polymeric passive samplers and ten compounds. A regression model of form **ln(*D*) = 0.707ln(*c1p*) - 2.7391** with an ***R2*= 0.9744** was obtained to relate the polymer-water partition coefficients (*D*) and concentration of hydrophobic organic compounds in passive sampler (***c1p***). It was also found that polymer-water partition coefficients are related to the concentration of hydrophobic organic compounds in water (***c1W***) as **ln(*D*) = 2.412ln(*c1p*) – 9.348.** Based on the results, the tie lines of concentration for hydrophobic organic compounds in passive sampler (***c1p***) and concentration of hydrophobic organic compounds in water (***c1W***) are in the form of **ln(*c1W*) = 0.293ln(*c1p*) + 2.734**. The composition of water sample, and the interaction parameters of dissolved compounds-water and dissolved compounds-polymer, temperature and etc. actively influence the values of partition coefficient. The discrepancy observed over experimental data can be simply justified based on the local condition of sampling sites which alter these effective factors.

Keywords: Polymer; water; partition coefficients; passive samplers; Hansen solubility

# Introduction

Nowadays, the water, its relatively cheap production and high recovery are of major concerns ([Bergmair, Metz et al. 2015](#_ENREF_5), [Gido, Friedler et al. 2016](#_ENREF_7), [Trapani, Polyzoidis et al. 2016](#_ENREF_22)) as water resources are limited and even would face reduction in the near future as the use and consumption of water is still high ([Hamiche, Stambouli et al. 2016](#_ENREF_8), [Lu, Zhang et al. 2016](#_ENREF_14)). Various technologies have been developed over last years for water purification and recovery from wastewater and polluted resources ([Mahmoud, Yosra et al. 2016](#_ENREF_15), [Xu, Bai et al. 2016](#_ENREF_26), [Zanacic, Stavrinides et al. 2016](#_ENREF_27)) and there is still ongoing researches for production of required water for our societies ([Wahlgren 2001](#_ENREF_24), [Bar 2004](#_ENREF_3), [Bergmair, Metz et al. 2014](#_ENREF_4), [Milani, Qadir et al. 2014](#_ENREF_16), [Bergmair, Metz et al. 2015](#_ENREF_5)).

Having regard to these investigations, higher regulation and health standards have been planned and subjected for industries and water consuming sectors to adhere in such a way to reduce the water pollution as a remedy to high cost of water production and purification. Analysis and measurement of contaminants (hydrophobic organic compounds in particular) present in water streams is then a first step for health risk level determination and technology selection for treatment purposes. Single-phase polymeric passive samplers have attracted much attention for measuring the concentration of hydrophobic organic compounds in water as the direct extraction is often laborious and expensive ([Adams, Lohmann et al. 2007](#_ENREF_2), [Rainer Lohmann and Muir 2009](#_ENREF_19), [Endo, Hale et al. 2011](#_ENREF_6), [Thompson, Hsieh et al. 2015](#_ENREF_20)). Polyoxymethylene (POM), Polydimethylsiloxane (PDMS) and low density polyethylene (LDPE) have been the most widely used polymers for passive samplers ([Thompson, Hsieh et al. 2015](#_ENREF_20)).

Due to the cost and time associated with the experimental researches, development of a predictive method for estimation and evaluation of polymeric passive samplers’ performance for various hydrophobic organic compounds is highly needed and valuable. Mathematical modeling of unit operations has been a valuable tool to obtain a more clear understanding of processes and influencing parameters prior to any experimental study and results in time and cost savings ([Tosun 2007](#_ENREF_21), [Khansary, Joogh et al. 2014](#_ENREF_11)). Having a well-established model, one might investigate the effect of various operating parameters and evaluate design scenarios.

Performance and suitability of polymeric passive sampler for identification and measurement of hydrophobic organic compounds, in particular, presented in water can be evaluated and assessed by determination of polymer-water partition coefficients. The polymer-water partition coefficients have been experimentally measured for various polymeric passive samplers and data are reported in literature ([Adams, Lohmann et al. 2007](#_ENREF_2), [Rainer Lohmann and Muir 2009](#_ENREF_19), [Endo, Hale et al. 2011](#_ENREF_6), [Thompson, Hsieh et al. 2015](#_ENREF_20)). However, discrepancy can be observed over experimental data for different sampling sites. The cost of experiments, raw materials purchase and preparations, facility and equipment maintenance and etc., might be reduced provided that a theoretical analysis could be performed to check the suitability and feasibility of selected raw polymeric materials for fabrication of polymeric passive samplers.

For this purpose, in this work, following the fundamental chemical thermodynamic equations governing the concerned local equilibrium ([J.M. Smith, H. Van Ness et al. 2005](#_ENREF_10)), successful attempts were made to establish a theoretical model of polymer-water partition coefficients in which Flory–Huggins model based on the Hansen solubility parameters was used for calculation of activity coefficient as illustrated in the following sections.

# Partition coefficient model

By contacting the aqueous and polymeric phases, a local thermodynamic equilibrium will be established at the interface of these two phases. The chemical potentials of compound of interest in two contacting phases must be equal at operating conditions i.e. temperature and pressure as given in Eq. 1. Superscripts *W* and *P* denotes aqueous and polymeric phases, respectively. Subscript 1 denotes the compound of interest. *μ* denotes the chemical potential and Δ accounts for the change in chemical potential referring to a reference state ([J.M. Smith, H. Van Ness et al. 2005](#_ENREF_10)).

|  |  |
| --- | --- |
|  | 1 |

Employing the same reference state for both phases ([J.M. Smith, H. Van Ness et al. 2005](#_ENREF_10)), Eq. 1 can be rewritten as given by Eq. 2.

|  |  |
| --- | --- |
|  | 2 |

Here, *x* denotes the mole fraction of compound of interest and γ denotes the activity coefficient of compound of interest.

For calculation of activity coefficient of compound of interest, there is a wide variety of models to be used ([J.M. Smith, H. Van Ness et al. 2005](#_ENREF_10)). A Flory–Huggins model based on the Hansen solubility parameters was used here for calculation of activity coefficient which for binary mixtures is given by Eq. 3 ([Lindvig, Michelsen et al. 2002](#_ENREF_13)) where  and  are the volume fractions and mole fractions and  is the composition independent Flory–Huggins interaction parameter between compound of interest and compound 2 (water or polymer) which is given by Eq. 4 ([Lindvig, Michelsen et al. 2002](#_ENREF_13)) where *V1* is molar volume of compound of interest, *R* is the universal gas constant and *T* is temperature.

|  |  |
| --- | --- |
|  | 3 |
|  | 4 |

Where  denotes dispersion part of Hansen solubility parameter,  denotes polar part of Hansen solubility parameter, and  hydrogen-bonding part of Hansen solubility parameter ([Lindvig, Michelsen et al. 2002](#_ENREF_13)).

Using Eq. 3, one might write Eq. 5 ([Khansary, Mellat et al. 2017](#_ENREF_12));

|  |  |
| --- | --- |
|  | 5 |

Thus, Eq. 2 reads Eq. 6;

|  |  |
| --- | --- |
|  | 6 |

One might write ([Khansary, Mellat et al. 2017](#_ENREF_12)). Thus, Eq. 6 simplifies to Eq. 7;

|  |  |
| --- | --- |
|  | 7 |

By defining partition coefficient as ([Khansary, Mellat et al. 2017](#_ENREF_12)), Eq. 7 can be simplified as Eq.8;

|  |  |
| --- | --- |
|  | 8 |

Rearranging Eq.8 in power orders of, one would obtain;

|  |  |
| --- | --- |
|  | 9 |
|  | 10 |

The solutions for cubic equations same as equation above (Eq. 10) have been given by Spiegel and Liu ([Murray R. Spiegel and Liu 1999](#_ENREF_17)). Model application follows following steps;

**Step 1**: select compound 1 for which the polymer-water partition coefficient must be found and determine its chemical structure,

**Step 2**: calculate ,  and  using either chemical structure or available data in literatures such as Ref. ([Hansen 2000](#_ENREF_9)),

**Step 3**: calculate *V1*, *Mw1* and *ρ1* using either chemical structure or available data in literature such as Ref. ([Poling, Prausnitz et al. 1987](#_ENREF_18), [2010](#_ENREF_1)),

**Step 4**: using Eq. 4, calculate and at temperature of interest,

**Step 5**: for each guess of *D* value, find solutions for Eq. 10,

**Step 6**: convert calculated  to  using,

# Validation of proposed method

For validation of the proposed method, three polymeric passive samplers and ten compounds were considered and relevant data were collected from literature ([Adams, Lohmann et al. 2007](#_ENREF_2), [Rainer Lohmann and Muir 2009](#_ENREF_19), [Endo, Hale et al. 2011](#_ENREF_6), [Thompson, Hsieh et al. 2015](#_ENREF_20)). The required properties of water are listed in Table 1. The required properties of selected polymeric passive samplers are listed in Table 2. The required properties of selected organic compounds are listed in Table 3.

Table . Properties of water (values collected from Ref. ([Hansen 2000](#_ENREF_9)))

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Compounds** | **δd (MPa0.5)** | **δp (MPa0.5)** | **δh (MPa0.5)** | ***Mw* (gr/mol)** | ***ρ* (gr/cm3)** |
| water | 15.5 | 16 | 42.3 | 18.0153 | 1 |

Table 2. Properties of polymers used as passive samplers (values collected from Ref. ([Hansen 2000](#_ENREF_9), [van Krevelen and Nijenhuis 2008](#_ENREF_23)))

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Compounds** | **δd (MPa0.5)** | **δp (MPa0.5)** | **δh (MPa0.5)** | ***Mw* (gr/mol)** | ***ρ* (gr/cm3)** |
| Polyethylene (LDPE) | 17.50 | 4.30 | 8.30 | 28.1 | 0.94 |
| Polydimethylsiloxane (PDMS) | 16.86 | 0.12 | 8.60 | 74.1 | 0.98 |
| Polyoxymethylene (POM) | 17.2 | 9.2 | 9.8 | 30.1 | 1.41 |

Table . Properties of selected dissolved compounds ([Hansen 2000](#_ENREF_9), [2010](#_ENREF_1), [Wohlfarth 2010](#_ENREF_25), [Khansary, Mellat et al. 2017](#_ENREF_12))

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **Compounds** | **δd (MPa0.5)** | **δp (MPa0.5)** | **δh (MPa0.5)** | ***Mw* (gr/mol)** | ***ρ* (gr/cm3)** | ***V* (cm3/mol)** |
| Phenanthrene | 9.4 | 1.0 | 1.9 | 178.23 | 1.18 | 110.51 |
| Pyrene | 23.50 | 5.76 | 3.72 | 252.31 | 1.7 | 148.4 |
| Chrysene | 23.72 | 4.70 | 2.86 | 219.96 | 1.27 | 173.2 |
| Perylene | 25.41 | 5.94 | 2.88 | 252.32 | 1.43 | 176.0 |
| Anthracene | 21.81 | 4.53 | 3.71 | 178.23 | 1.25 | 142.54 |
| Caffeine | 19.5 | 10.1 | 13 | 194.19 | 1.23 | 157.87 |
| Phenol | 18 | 5.9 | 14.9 | 94.11 | 1.07 | 87.95 |
| Acetanilide | 20.6 | 13.3 | 12.4 | 135.17 | 1.22 | 110.79 |
| Carbazole | 21.7 | 6.4 | 6.2 | 167.206 | 1.3 | 128.16 |
| Estrone | 18.48 | 3.96 | 9.74 | 270.37 | 1.16 | 232.10 |

The calculated and at temperature of experiments mentioned in reference works ([Adams, Lohmann et al. 2007](#_ENREF_2), [Rainer Lohmann and Muir 2009](#_ENREF_19), [Endo, Hale et al. 2011](#_ENREF_6), [Thompson, Hsieh et al. 2015](#_ENREF_20)) are listed in Table 4.

Table . Calculated and values

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Compounds** | **T (°C)** |  |  | | |
| LDPE | PDMS | POM |
| Phenanthrene | 24 | 13.46 | 2.11 | 1.80 | 2.50 |
| Pyrene | 24 | 16.66 | 1.51 | 2.09 | 1.87 |
| Chrysene | 24 | 20.54 | 1.94 | 2.55 | 2.51 |
| Perylene | 24 | 21.88 | 3.02 | 3.84 | 3.51 |
| Anthracene | 10 | 16.17 | 0.87 | 1.28 | 1.31 |
| Caffeine | 25 | 9.15 | 0.69 | 1.40 | 0.31 |
| Phenol | 25 | 4.67 | 0.25 | 0.42 | 0.21 |
| Acetanilide | 25 | 6.74 | 0.91 | 1.64 | 0.47 |
| Carbazole | 25 | 12.01 | 0.62 | 1.08 | 0.79 |
| Estrone | 25 | 17.42 | 0.08 | 0.37 | 0.48 |

The overall relationship between concentrations and partition coefficients for all studied systems is shown in Fig. 1. For each polymeric passive sampler and the dissolved compounds considered, the results are provided in **supplementary online file** individually. A regression model of the form **ln(*D*) = 0.707ln(*c1p*) - 2.7391** with an ***R2*= 0.9744** was obtained by fitting of reported in Fig. 1 to relate the polymer-water partition coefficients (*D*) and concentration of hydrophobic organic compounds in passive sampler (***c1p***). It was also found that polymer-water partition coefficients are related to the concentration of hydrophobic organic compounds in water (***c1W***) as **ln(*D*) = 2.412ln(*c1p*) – 9.348.** Based on the results, the tie lines of concentration of hydrophobic organic compounds in passive sampler (***c1p***) as well as concentration of hydrophobic organic compounds in water (***c1W***) are in the form of **ln(*c1W*) = 0.293ln(*c1p*) + 2.734**.

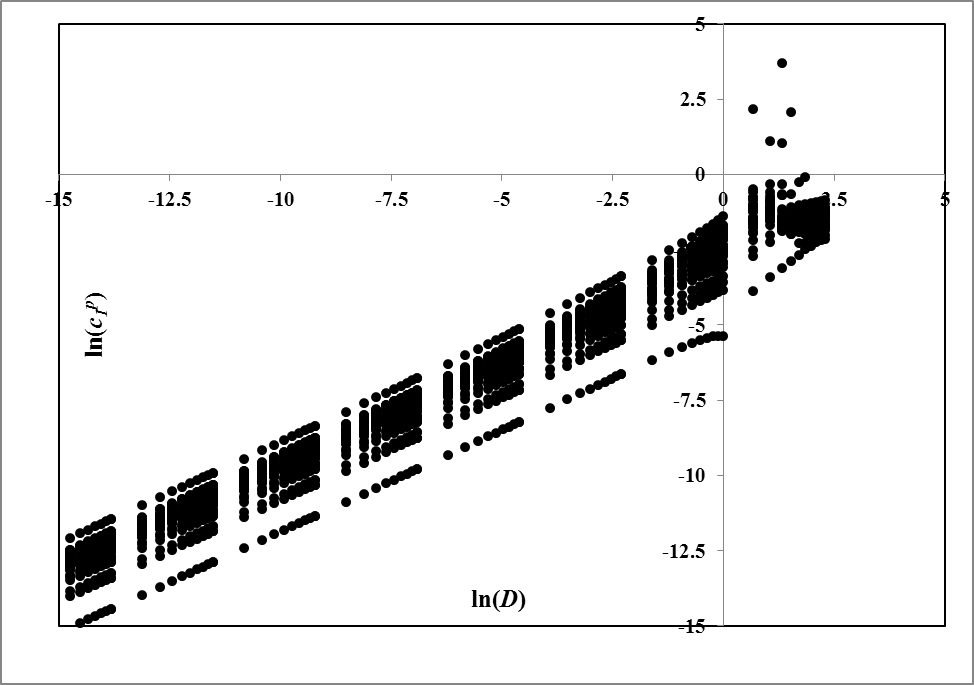


Fig. 1. Overall relationship between concentrations and partition coefficients for all studied systems

Following the presented theoretical approach or the final inspired relationships, it is of easiest task to get an approximate of a nominated polymer intended to be used as a passive sampler. Using the regression model, it is possible to decline inappropriate material selection in just little of computations. Obviously, the partition coefficient of any polymer-water sample can be determined using the concentration of compound within the passive sample and consequently, one might simply calculate the concentration of dissolved compound in water. Reported values of partition coefficients that are determined experimentally showed different values compared to literature ([Adams, Lohmann et al. 2007](#_ENREF_2), [Rainer Lohmann and Muir 2009](#_ENREF_19), [Endo, Hale et al. 2011](#_ENREF_6), [Thompson, Hsieh et al. 2015](#_ENREF_20)) because as it is evidence from the thermodynamic analysis presented here, that the composition of water sample, and the interaction parameters of dissolved compounds-water and dissolved compounds-polymer, temperature and etc. influence the values of partition coefficient. The method presented here can be simply applied and is supported with fundamental thermodynamic basis, which makes it a reliable and cost-competitive method for interoperation of dissolved compounds concentration from the values detected by passive samplers.

# Conclusions

Using a thermodynamic analysis, a theoretical approach was established based on the fundamental principal of chemical thermodynamic equilibrium with a well-studied and well-suited model (Flory-Huggins). A simple and easy-to-use method was developed for calculation of polymer-water partition coefficients for application in polymeric passive samplers. The method explicitly shows the influence of physicochemical properties of water, polymer and the dissolved compounds as well as their interactions on the partition coefficient. The discrepancy observed over experimental data can be simply justified based on the local condition of sampling sites.

References

(2010). CRC Handbook of Chemistry and Physics, CRC Press.

Adams, R. G., R. Lohmann, L. A. Fernandez and J. K. MacFarlane (2007). "Polyethylene Devices:  Passive Samplers for Measuring Dissolved Hydrophobic Organic Compounds in Aquatic Environments." Environmental Science & Technology **41**(4): 1317-1323.

Bar, E. (2004). "Extraction of water from air — an alternative solution for water supply." Desalination **165**: 335.

Bergmair, D., S. J. Metz, H. C. de Lange and A. A. van Steenhoven (2014). "System analysis of membrane facilitated water generation from air humidity." Desalination **339**: 26-33.

Bergmair, D., S. J. Metz, H. C. de Lange and A. A. van Steenhoven (2015). "A low pressure recirculated sweep stream for energy efficient membrane facilitated humidity harvesting." Separation and Purification Technology **150**: 112-118.

Endo, S., S. E. Hale, K. U. Goss and H. P. Arp (2011). "Equilibrium partition coefficients of diverse polar and nonpolar organic compounds to polyoxymethylene (POM) passive sampling devices." Environ Sci Technol **45**(23): 10124-10132.

Gido, B., E. Friedler and D. M. Broday (2016). "Assessment of atmospheric moisture harvesting by direct cooling." Atmospheric Research **182**: 156-162.

Hamiche, A. M., A. B. Stambouli and S. Flazi (2016). "A review of the water-energy nexus." Renewable and Sustainable Energy Reviews **65**: 319-331.

Hansen, C. M. (2000). Hansen solubility parameters: a user’s handbook. Florida, CRC Press.

J.M. Smith, H. Van Ness and M. Abbott (2005). Introduction to Chemical Engineering Thermodynamics. New York, McGraw-Hill.

Khansary, M. A., F. K. Q. Joogh, A. Hosseini, J. Safari, E. Allahyari, N. S. Zadeh and A. H. Sani (2014). "Modeling Drying of a Coated Paper." International Journal of Modeling, Simulation, and Scientific Computing **05**(01): 1350019.

Khansary, M. A., M. Mellat, S. H. Saadat, M. Fasihi-Ramandi, M. Kamali and R. A. Taheri (2017). "An enquiry on appropriate selection of polymers for preparation of polymeric nanosorbents and nanofiltration/ultrafiltration membranes for hormone micropollutants removal from water effluents." Chemosphere **168**: 91-99.

Lindvig, T., M. L. Michelsen and G. M. Kontogeorgis (2002). "A Flory–Huggins model based on the Hansen solubility parameters." Fluid Phase Equilibria **203**(1-2): 247-260.

Lu, S., X. Zhang, H. Bao and M. Skitmore (2016). "Review of social water cycle research in a changing environment." Renewable and Sustainable Energy Reviews **63**: 132-140.

Mahmoud, B., M. Yosra and A. Nadia (2016). "Effects of magnetic treatment on scaling power of hard waters." Separation and Purification Technology **171**: 88-92.

Milani, D., A. Qadir, A. Vassallo, M. Chiesa and A. Abbas (2014). "Experimentally validated model for atmospheric water generation using a solar assisted desiccant dehumidification system." Energy and Buildings **77**: 236-246.

Murray R. Spiegel and J. Liu (1999). Mathematical Handbook of Formulas and Tables, McGraw Hill Professional.

Poling, B. E., J. M. Prausnitz and J. P. O'Connell (1987). Properties of Gases and Liquids, McGraw-Hill Professional.

Rainer Lohmann and D. Muir (2009). "Global Aquatic Passive Sampling (AQUA-GAPS): Using Passive Samplers to Monitor POPs in the Waters of the World." Environ Sci Technol **44**(3): 860–864.

Thompson, J. M., C. H. Hsieh and R. G. Luthy (2015). "Modeling uptake of hydrophobic organic contaminants into polyethylene passive samplers." Environ Sci Technol **49**(4): 2270-2277.

Tosun, I. (2007). Modeling in Transport Phenomena : A Conceptual Approach, Elsevier.

Trapani, F., A. Polyzoidis, S. Loebbecke and C. G. Piscopo (2016). "On the general water harvesting capability of metal-organic frameworks under well-defined climatic conditions." Microporous and Mesoporous Materials **230**: 20-24.

van Krevelen, D. W. and K. T. Nijenhuis (2008). Properties of Polymers: Their Correlation with Chemical Structure; Their Numerical Estimation and Prediction from Additive Group Contributions, Elsevier.

Wahlgren, R. V. (2001). "Atmospheric water vapour processor designs for potable water production: a review." Water Research **35**(1): 1-22.

Wohlfarth, C. (2010). Polymers: Group VIII: Advanced Materials and Technologies. Germany, Springer-Verlag Berlin Heidelberg.

Xu, M., X. Bai, L. Pei and H. Pan (2016). "A research on application of water treatment technology for reclaimed water irrigation." International Journal of Hydrogen Energy **41**(35): 15930-15937.

Zanacic, E., J. Stavrinides and D. W. McMartin (2016). "Field-analysis of potable water quality and ozone efficiency in ozone-assisted biological filtration systems for surface water treatment." Water Research **104**: 397-407.