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Quantifying hydrophobicity of natural organic matter using partition coefficients in aqueous two-phase systems

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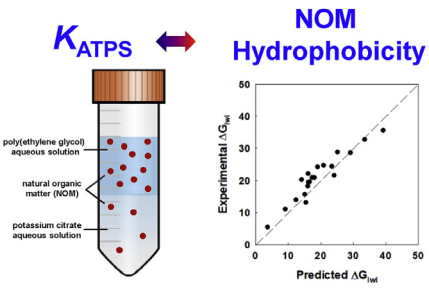
HIGHLIGHTS

- An aqueous two-phase system (ATPS) is designed to scale NOM hydrophobicity.
- Partition coefficients in ATPS (K_{ATPS}) is a quantitative measure of NOM hydrophobicity.
- The model based K_{ATPS} gives sound prediction of NOM hydrophobicity in natural waters.
- ATPS scale system is simple, low-cost, and suitable for routine measurements.

GRAPHICAL ABSTRACT



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ABSTRACT

The hydrophobicity of natural organic matter (NOM) is of great significance for its interfacial processes in natural and engineered systems. However, there is no well-accepted method for the routine determination of NOM hydrophobicity. In this study, the hydrophobicity of NOM spanning a wide range of origins and properties was quantified based on their partition coefficients (K_{ATPS}) in poly (ethylene glycol)/potassium citrate aqueous two-phase systems (ATPS). The LnK_{ATPS} of NOM correlated well with the elemental, structural, and thermodynamic indices commonly used to characterize NOM hydrophobicity, including (O + N)/C, O/C, aromatic and aliphatic carbon, and the free energy of interactions between molecules (ΔG_{iwi}). A simple linear model was developed to predict NOM hydrophobicity using K_{ATPS}. The model was validated using 20 natural water samples collected from rivers and lakes, which suggested good prediction power. ATPS scale system is simple, fast, low-cost, environmentally friendly, and requires little pretreatment and small sample volume. Overall, K_{ATPS} can be used as quantitative measure of NOM hydrophobicity that facilitates routinely characterizing the interfacial properties of NOM.

1. Introduction

Natural organic matter (NOM) is ubiquitous in terrestrial and aquatic environments. The hydrophobicity of NOM is one of its most fundamental properties which affects many geochemical and engineered processes of environmental significance. It impacts the

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partitioning of organic pollutants to NOM, influencing their fate and transport as well as bioavailability (Chiou et al., 1979; Kukkonen and Oikari, 1991; Luthy et al., 1997). It affects the sorption of NOM on geosorbents and its aggregation behavior, playing an important role in the cycling and export of carbon and other elements (Meier et al., 1999; Wang and Xing, 2005; Xu et al., 2017). From the engineering perspective, the hydrophobicity of NOM influences the performance of many water treatment unit processes, such as fouling of membrane systems and formation of disinfection byproducts (Hong and Elimelech, 1997; Kennedy et al., 2005; Liu and Zhang, 2014; Pan and Zhang, 2013; Yang and Zhang, 2013).

The hydrophobicity of NOM is not easily quantifiable. Current approaches include fractionation, elemental analysis, nuclear magnetic resonance (NMR) analysis, and reverse-phase high performance liquid chromatography (HPLC). The adsorption of NOM to XAD resins was initially used to isolate NOM from natural waters. It also can be applied to separate the hydrophobic, transphilic, and hydrophilic fractions of NOM, whose percentages provide a sense of the overall hydrophobicity (Croué et al., 2003; Thacker et al., 2005). The fractionation method is operational and labor- and time-intensive. The elemental composition of NOM (e.g., O/C and (O + N)/C) is commonly used in the literature for characterizing NOM polarity/hydrophobicity (Grathwohl, 1990; Kang and Xing, 2005; Xing, 1997). However, this method needs significant amount of isolated NOM powder sample, which requires large effort to concentrate, isolate, and purify NOM from waters and soils. Solid-state ^{13}C NMR is a powerful tool for quantitatively characterizing the structure of NOM. The structural components such as aromatic and aliphatic carbons of NOM were reported to correlate to its sorption capacity of polycyclic aromatic hydrocarbons (Gauthier et al., 1987; Chefetz and Xing, 2009; Perminova et al., 1999; Peuravuori, 2001), which reflected its hydrophobicity. Nevertheless, this approach requires sophisticated analytical instruments and experienced personal. For characterizing aquatic NOM, the solid-state NMR analysis also needs significant amount of isolated NOM powder sample. Reverse-phase HPLC can be used to measure the polarity/hydrophobicity distribution of NOM components based on the dynamic equilibrium processes between NOM components and the stationary phase (Egeberg and Alberts, 2002; Namjesnik-Dejanovic and Cabaniss, 2004; Xing et al., 2012). However, it still relies on instruments and influenced by the choice of reference substances as well as the operation conditions (Klein et al., 1988; Namjesnik-Dejanovic and Cabaniss, 2004). Furthermore, this approach is not able to quantify the overall hydrophobicity of NOM. Some spectroscopic indicators were reported to correlate to the aromaticity of NOM, such as $SUVA_{254}$, E_4/E_6, and humification index (Hur et al., 2009; Summers et al., 1987; Senesi et al., 1989; Weishaar et al., 2003; Wang and Chen, 2018). However, these indirect correlations are not very reliable for quantitatively scale NOM hydrophobicity. So far, there is no well-accepted standard method for the routine determination of NOM hydrophobicity.

The standard measurement of compound hydrophobicity is commonly based on its partition behavior in two-phase systems. The *n*-octanol-water system usually used for characterizing hydrophobicity of organic compounds is not suitable for NOM which is comprised of a continuum of molecules, macromolecules, and supermolecules with considerable hydrophilicity. Here, we propose the use of aqueous two-phase systems (ATPS) as a simple and reliable approach to quantify NOM hydrophobicity. ATPS are formed by mixing of two polymers or a polymer and a salt in water (Hatti-Kaul, 2001). They are previously used for separation and purification of biological materials (e.g., cells, membranes, and proteins) owing to their biocompatibility, simplicity, and low-cost (Asenjo and Andrews, 2011; Hatti-Kaul, 2001; Iqbal et al., 2016). The major properties of biomolecules that affect their partition in ATPS are hydrophobicity, surface charge, size, conformation, and bio-specific affinity (Asenjo and Andrews, 2011; Grilo et al., 2016). Among them, hydrophobic interactions play a key role in determining the partition coefficients (K_{ATPS}) (Andrews et al., 2005; Andrews and Asenjo, 2010; Asenjo and Andrews, 2011; Franco et al., 1996; Hachem et al., 1996). Previous studies showed that K_{ATPS} of proteins correlated with their hydrophobicity (Andrews et al., 2005; Andrews and Asenjo, 2010; Franco et al., 1996; Hachem et al., 1996). Accordingly, we hypothesize that K_{ATPS} is a practical measurement of NOM hydrophobicity.

In the present study, we examined this hypothesis using NOM samples that span a wide range of origins and physicochemical properties. A poly (ethylene glycol)/potassium citrate ATPS was used for NOM characterization. The K_{ATPS} of NOM was correlated to elemental, structural, and thermodynamic indices to examine its ability to quantify hydrophobicity. The applicability of this scale system was further validated using a set of natural water samples. Our objective was to establish a quantitative scale system for the hydrophobicity of NOM using ATPS.

2. Materials and methods

2.1. Materials

Poly (ethylene glycol) (PEG, BioUltra, M_w 10000) was purchased from Sigma-Aldrich, USA. Analytical-grade potassium citrate tribasic monohydrate, citric acid monohydrate, sodium hydroxide, and hydrochloric acid were purchased from Sinopharm Chemical Reagent Co., Ltd., China. Deionized water (18.2 MΩ cm resistivity at 25 °C) was produced by an ELGA Labwater system (PURELAB Ultra, ELGA LabWater Global Operations, UK) and was used for all the experiments.

Suwannee River NOM (SR NOM, 2R101 N), Upper Mississippi River NOM (UM NOM, 1R110 N), Nordic Lake NOM (NL NOM, 1R108 N), Suwannee River fulvic acid (SR FA, 2S101F), Pahokee Peat FA (PP FA, 2S103F), Suwannee River humic acid (SR HA, 3S101H), Elliott Soil HA (ES HA, 4S102H), Pahokee Peat HA (PP HA, 1S103H), and Leonardite HA (LEO HA, 1S104H) were provided by the International Humic Substances Society (IHSS, USA). A homemade HA (LN HA) was extracted from the surface soil (0–20 cm) collected from Shenyang, Liaoning Province in northeast China using a standard method (Sparks et al., 1996; Sun et al., 2010). The elemental compositions and the ^{13}C NMR estimates of carbon distribution for the NOM are summarized in Table S1 and S2, respectively.

The NOM stock solution was prepared by dissolving a predetermined amount of NOM powder in deionized water. After adjusted pH to ~6.8, the solution was filtered through a 0.45-μm membrane (Supor-450, Pall, USA). The concentration of the NOM stock solution was determined by a total organic carbon (TOC) analyzer (vario TOC, Elementar, Germany). The stock solutions were stored at 4 °C in dark before the experiments.

2.2. Partition coefficients in ATPS (K_{ATPS})

The PEG/potassium citrate ATPS is made of aqueous PEG and potassium citrate solutions. The top phase is aqueous 50% (w/w) PEG solution, and the bottom phase is aqueous 40% (w/w) potassium citrate solution. The pH of potassium citrate solution was adjusted to 7.0 using 40% (w/w) citric acid solution prior to use. Partition experiments of NOM were performed in 15 mL graduated centrifuge tubes with 4 mL PEG, 4 mL potassium citrate, and 2 mL NOM solution (~15 mgC/L) or natural water samples (see the workflow in Fig. 1). The systems were thoroughly mixed by a vortex

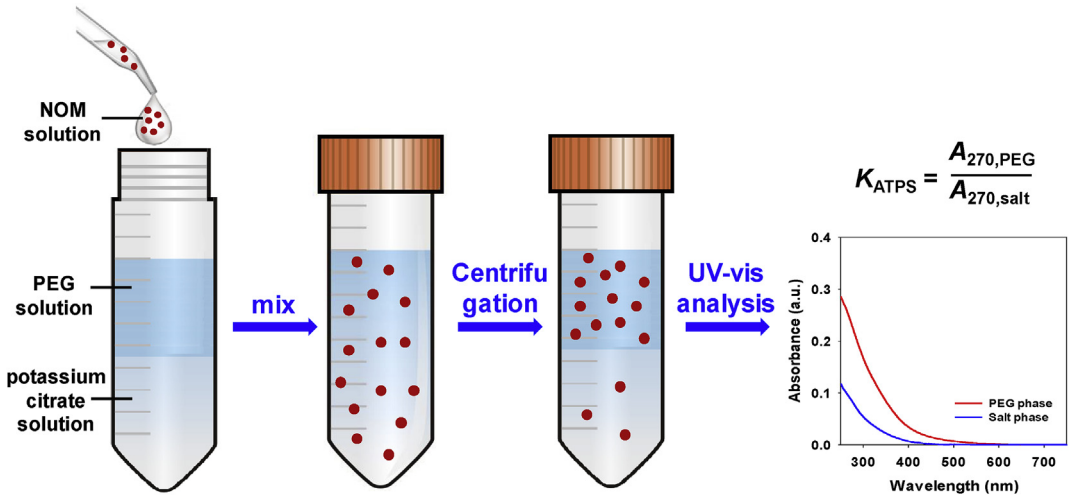

Fig. 1. Workflow showing the steps involved in determining the partition coefficients of NOM in aqueous two-phase system (K_{ATPS}).

shaker and continuously mixed in a shaker (ZQLY-180GF, Zhichu, China) at 150 rpm and 20 °C for 50 min. This period of time was sufficient to reach partition equilibrium of NOM according to the kinetic data (see Fig. S1 in supplementary information/SI). After centrifugation at 4500 rpm (relative centrifugal force 2149 g, Cence H1850R, Xiangyi Instrument, China) for 5 min, both top and bottom phases were sampled for absorbance measurements at 270 nm using a UV-2700 UV–Vis spectrophotometer (SHIMADZU, Japan) in a 3-cm quartz cuvette. A control sample was carried out using the same treatment with the addition of 2 mL DI water instead of NOM solution. The background absorbances of PEG and potassium citrate solutions in the control sample at 270 nm were subtracted from other sample measurements. The K_{ATPS} was calculated by the ratio of the absorbance of top phase to that of bottom phase. It is worth noting that K_{ATPS} does not equal to the concentration ratio of NOM in these two phases. More hydrophobic molecules in NOM tend to accumulate in the PEG phase. They are expected to absorb UV light more efficiently than the hydrophilic NOM molecules in the salt phase due to their more unsaturated structure (Helms et al., 2014; Summers et al., 1987). Thus, the calculated K_{ATPS} is expected to be higher than the ratio of NOM concentration in top phase to that in bottom phase. It also does not account for the distribution of non-chromophores such as aliphatic carbons. The full scan of NOM in both phases have no absorbance at wavelength longer than 700 nm, indicating there is no light scattering due to colloidal particles (Fig. S2 in SI). The measurement of K_{ATPS} for reference NOM sample was done in triplicate and the relatively standard deviations (RSD) was within 2.2%.

2.3. Calculation of the free energy of interactions between NOM molecules in water (ΔG_{iwi})

The hydrophobicity of molecules can be evaluated using the free energy of interactions between NOM molecules in water (ΔG_{iwi}) using equation (2) (van Oss, 1995):

$$\Delta G_{iwi} = -2\left(\gamma_i^{LW} - \gamma_w^{LW}\right)^2 - 4\left(\sqrt{\gamma_i^+\gamma_i^-} + \sqrt{\gamma_w^+\gamma_w^-} - \sqrt{\gamma_i^+\gamma_w^-} - \sqrt{\gamma_i^-\gamma_w^+}\right) \quad (2)$$

where the subscript i represents NOM and w represents water. γ^{LW} is the Lifshitz-van der Waals component which includes the dispersion, induction, and orientation contributions to the van der Waals interactions (van Oss et al., 1988). γ^+ and γ^- are the electron-acceptor and electron-donor parameters of the polar surface tension component, respectively. For NOM, the values of γ_i^{LW}, γ_i^+ and γ_i^- can be determined by solving Young-Dupré equation (Equation (3)) (van Oss et al., 1988). Three different probe liquids (water, glycerol, and *n*-decane) with known surface tension parameters were used to measure the air-liquid-NOM contact angles (θ).

$$\gamma_p^{Tot}(1+\cos\theta) = 2\left(\sqrt{\gamma_i^{LW}\gamma_p^{LW}} + \sqrt{\gamma_p^+\gamma_i^-} + \sqrt{\gamma_i^+\gamma_p^-}\right) \quad (3)$$

where γ^{Tot} is the total surface tension. The subscript p represents the liquid used for contact angle measurement, including water ($\gamma_w^{Tot} = 72.8$, $\gamma_w^{LW} = 21.8$, and $\gamma_w^+ = \gamma_w^- = 25.5$ mJ m^{-2}), glycerol ($\gamma_g^{Tot} = 64.0$, $\gamma_g^{LW} = 34.0$, $\gamma_g^+ = 3.92$ and $\gamma_g^- = 25.5$ mJ m^{-2}), and *n*-decane ($\gamma_d^{Tot} = 23.8$, $\gamma_d^{LW} = 23.8$, $\gamma_d^+ = \gamma_d^- = 0$ mJ m^{-2}).

The NOM solution was filtered against an ultrafiltration membrane (3 kDa, Millipore Corporation, USA) using an ultrafiltration cell (Model 8010, Millipore Corporation, USA) to form a cake layer for contact angle measurements (Cho et al., 1998; Lee et al., 2004; Lin et al., 2014). The cake layer was dried by nitrogen gas under room temperature and subjected to static contact angle measurements. Static contact angles of three probe liquids including water, glycerol, and *n*-decane on the NOM cake layer were measured at least three times at different locations by an optical contact angle measuring device (OCA30, Dataphysics Instruments GmbH, Germany). We also used reverse osmosis membranes (Reverse Osmosis CE, GE Osmonics, USA) to form some of the NOM cake layers in a reverse osmosis system (HP4750, Sterlitech, USA) in order to avoid potential loss of NOM molecules during the filtration. The ΔG_{iwi} measured using ultrafiltration method was almost the same as that measured using reverse osmosis method (Fig. S3).

2.4. Collection of natural water samples

The natural water samples were collected from the rivers and lakes in Nanjing, China. The detailed sample information was summarized in Table S3 and Fig. 6a. All water samples were filtered through 0.45-μm membranes (Supor-450, Pall, USA) after collected and stored at 4 °C in dark. The samples were applied to K_{ATPS} analysis without any further pretreatment.

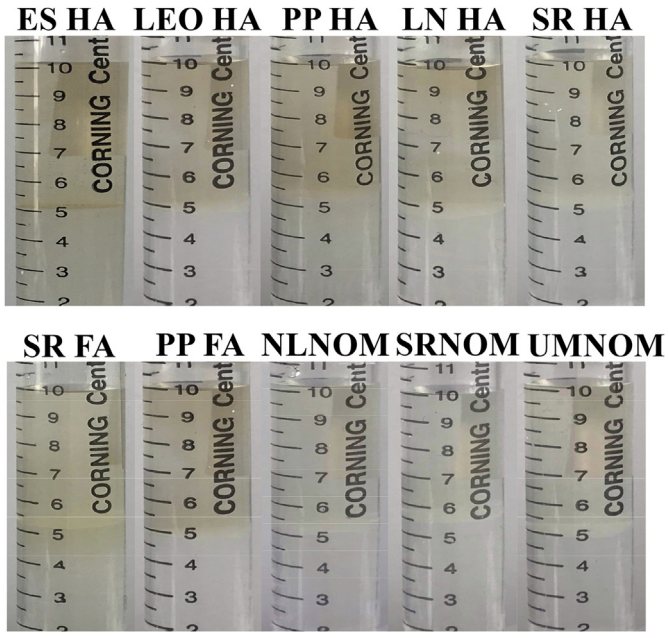

Fig. 2. Photographs of different NOM partitioning in the aqueous two-phase system. The top phase is comprised of aqueous PEG solution and the bottom phase is made of potassium citrate solution.

3. Results and discussion

3.1. Partition coefficient of NOM in aqueous two-phase systems

The workflow for determining the partition coefficients of NOM in ATPS (K_{ATPS}) is summarized in Fig. 1. The photographs of ATPS for characterizing NOM are shown in Fig. 2. The phase diagram of the PEG/potassium citrate system was determined (Fig. S4), which shows the boundary between the one-phase and two-phase regions (Asenjo and Andrews, 2011). The ATPS composition used in this study is above the binodal curve, indicating that the mixture will separate into two phases. Consistently, the ATPS shown in Fig. 2 separated into top and bottom phases with a clear interface. NOM with various origins and properties have different partition patterns between these two phases, which can be visualized in Fig. 2. The partition coefficients of NOM in ATPS (K_{ATPS}) are summarized in Table 1. They vary significantly from 0.91 (PP FA) to 7.18 (LEO HA), reflecting the diverse hydrophobicity of tested NOM. The average K_{ATPS} of all sample is 3.13 ± 2.04, suggesting that NOM generally tends to partition into the PEG phase. This process is mainly governed by hydrophobic interactions including the hydrophobicity effect and salting-out effect (Andrews and Asenjo, 1996; Asenjo and Andrews, 2011; Iqbal et al., 2016). As the PEG phase is more hydrophobic than the salt phase, hydrophobic NOM is more prone to partition into the PEG phase (i.e., hydrophobicity effect). The

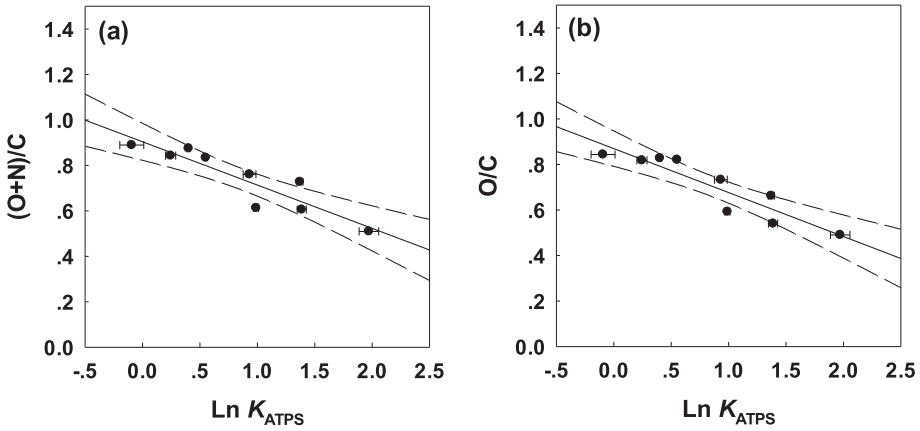

Fig. 3. Correlations between the partition coefficients of NOM in aqueous two-phase systems (K_{ATPS}) and the elemental ratios: (a) (O + N)/C and (b) O/C with regression line (solid line) and 95% confidence interval for regression (dashed lines). Error bars represent ± one standard deviation from the mean of triplicate samples.

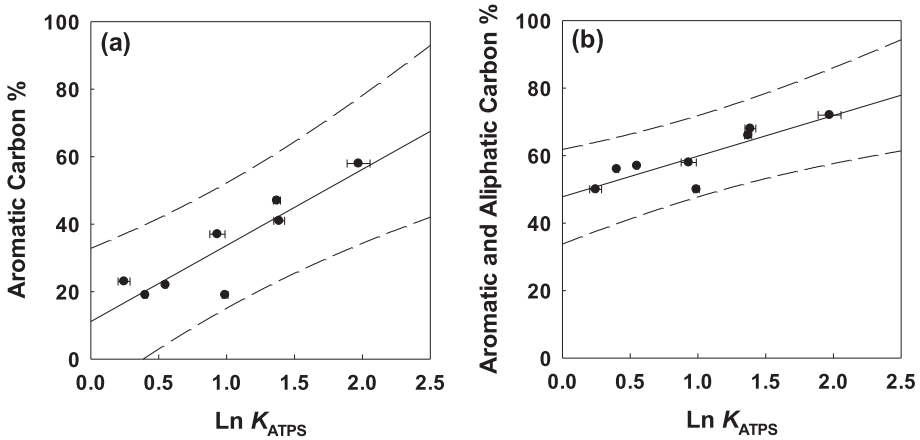

Fig. 4. Correlations between the partition coefficients of NOM in aqueous two-phase systems (K_{ATPS}) and the structural indices: (a) aromatic contents and (b) the sum of aromatic and aliphatic contents with regression line (solid line) and 95% confidence interval for regression (dashed lines). Error bars represent ± one standard deviation from the mean of triplicate samples.

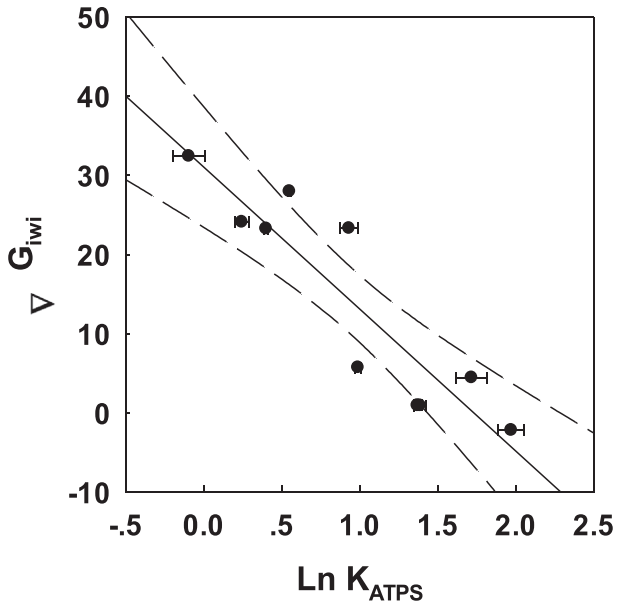

Fig. 5. Correlations between the partition coefficients of NOM in aqueous two-phase systems (K_{ATPS}) and the free energy of interactions between NOM molecules in water (ΔG_{iwi}) with regression line (solid line) and 95% confidence interval for regression (dashed lines). Error bars represent ± one standard deviation from the mean of triplicate samples.

presence of salt consumes the water in the salt phase and hence suppresses the hydration of NOM. Thus, the partition of NOM to more hydrophobic PEG phase is favored by the presence of salts (i.e., salting-out effect). The average K_{ATPS} of the humic acid, fulvic acid, and NOM subgroups are 4.65 ± 1.78, 1.32 ± 0.58, and 1.82 ± 0.76, respectively. The average K_{ATPS} of humic acid samples is higher than fulvic acid and NOM samples (Student's *t*-test, $p < 0.05$).

3.2. K_{ATPS} is a reliable quantitative measure of NOM hydrophobicity

The hydrophobicity of NOM is commonly characterized using the elemental composition and structural properties (Chefetz and Xing, 2009; Gauthier et al., 1987; Grathwohl, 1990; Kang and Xing, 2005; Xing, 1997). The NOM provided by the IHSS has the elemental composition and structural properties documented on their website (Table 1). The elemental composition of NOM provides insights on the abundance of polar moieties such as oxygen/nitrogen-containing functional groups. The atomic ratios (e.g., (O + N)/C and O/C) are often used to compare the hydrophobicity of different NOM (Grathwohl, 1990; Kang and Xing, 2005; Xing, 1997). A lower (O + N)/C or O/C ratio indicates lower polarity and hence higher hydrophobicity (Grathwohl, 1990; Kang and Xing, 2005; Xing, 1997). The correlations of LnK_{ATPS} with (O + N)/C and O/C were examined by linear regressions as shown in Fig. 3. Despite drastically different origins and structural properties of NOM, significant linear correlations ($p < 0.05$) were found between LnK_{ATPS} and (O + N)/C and O/C ($R^2 = 0.83$ and 0.85, respectively). The correlations can be described by following equations:

$$(O + N)/C = -0.190 \mathrm{Ln}K_{ATPS} + 0.904,\ R^2 = 0.83 \quad (4)$$

$$O/C = -0.193 \mathrm{Ln}K_{ATPS} + 0.870,\ R^2 = 0.85 \quad (5)$$

The NMR data provide further information on the structural properties of NOM. The aromatic and aliphatic carbon of NOM is often linked to its hydrophobicity and the ability to sorb organic compounds (Chefetz and Xing, 2009; Gauthier et al., 1987; Hur and Kim, 2009). As shown in Fig. 4, LnK_{ATPS} generally increases with increasing aromaticity as well as the sum of aromatic and aliphatic carbon contents of NOM (Equations (6) and (7)). LnK_{ATPS} increases with decreasing aliphatic carbon content due to the negative correlation between aromatic and aliphatic carbons in NOM (Fig. S5). However, there is significant scatter in the data because other structures, especially oxygen/nitrogen-containing moieties, are also important in determining NOM hydrophobicity.

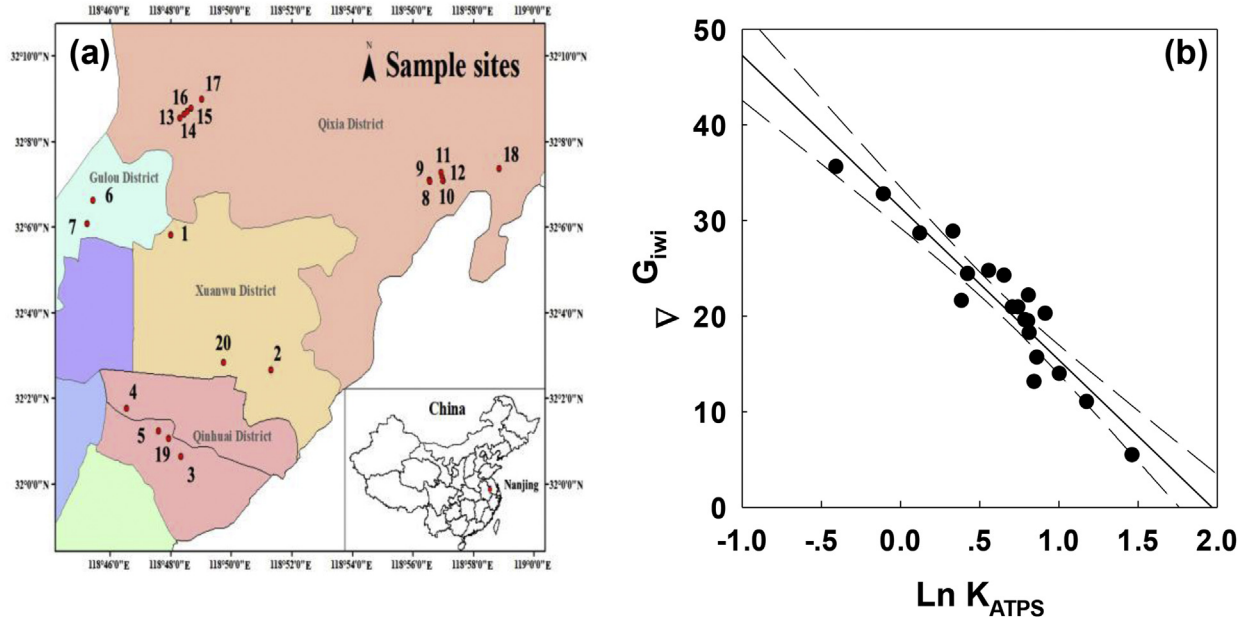

Fig. 6. Correlations between the partition coefficients of NOM in aqueous two-phase systems (K_{ATPS}) and the free energy of interactions between NOM molecules (ΔG_{iwi}) in natural water samples with regression line (solid line) and 95% confidence interval for regression (dashed lines). The water samples were collected from rivers and lakes in Nanjing, China. Detailed sample information can be found in the map and SI.

Table 1
Summary of the partition coefficients in aqueous two-phase systems (K_{ATPS}), elemental, structural, and thermodynamic properties of NOM.

NOM	K_{ATPS}	(O + N)/C [a]	O/C [a]	Aromatic Carbon% [a]	Aliphatic Carbon% [a]	ΔG_{iwi} (mJ m^{-2})
ES HA	4.00	0.61	0.54	41	27	0.91
LEO HA	7.18	0.51	0.49	58	14	−2.19
PP HA	3.94	0.73	0.66	47	19	0.94
LN HA	5.57	N.D.[b]	N.D.	N.D.	N.D.	4.44
SR HA	2.54	0.76	0.73	37	21	23.33
SR FA	1.73	0.83	0.82	22	35	27.98
PP FA	0.91	0.89	0.84	N.D.	N.D.	32.44
NL NOM	2.69	0.61[c]	0.59[c]	19	31	5.72
SR NOM	1.28	0.84	0.82	23	27	24.13
UM NOM	1.49	0.88	0.83	19	37	23.29

[a] Data from International Humic Substance Society Website (http://humic-substances.org/).
[b] Not determined.
[c] From Tanaka et al. (2005).

$$\text{Aromatic Carbon (\%)} = 22.570\text{Ln}K_{ATPS} + 11.123,\ R^2 = 0.80 \quad (6)$$

$$\text{Aromatic and Aliphatic Carbon (\%)} = 12.034\text{Ln}K_{ATPS} + 47.828,\ R^2 = 0.73 \quad (7)$$

Thermodynamically, the hydrophobicity of molecules/colloids can be evaluated by the free energy of interactions between these molecules/colloids in water, ΔG_{iwi} (van Oss, 1995). The calculated ΔG_{iwi} of NOM based on the contact angle measurements and Young-Dupré equation are summarized in Table 1. The contact angles and surface tension components for each NOM are summarized in Table S4. Hydrophobic molecules have $\Delta G_{iwi} < 0$ mJ m^{-2}, whereas hydrophilic ones have $\Delta G_{iwi} > 0$ mJ m^{-2}. Molecules with lower ΔG_{iwi} possess stronger hydrophobicity. Thus, most of NOM tested in this work are hydrophilic in nature except for LEO HA which has $\Delta G_{iwi} = -2.19$ mJ m^{-2}. It can be classified as partly hydrophobic (i.e., -84 mJ m$^{-2} < \Delta G_{iwi} < 0$ mJ m^{-2}) (van Oss, 1995). LnK_{ATPS} was found to increase with decreasing ΔG_{iwi} as shown in Fig. 5. Furthermore, a good linear correlation was found between LnK_{ATPS} and ΔG_{iwi} ($R^2 = 0.83$). The correlation can be described by the following equation:

$$\Delta G_{iwi} = -18.980\text{Ln}K_{ATPS} + 31.516,\ R^2 = 0.83 \quad (8)$$

Overall, the strong correlations between K_{ATPS} and these elemental/structural/thermodynamic indices collectively suggest that the hydrophobicity of NOM can be well quantified by K_{ATPS}.

3.3. Prediction model for the hydrophobicity of NOM in natural water samples based on K_{ATPS}

The ATPS scale system was further tested using 20 natural water samples collected from rivers and lakes in Nanjing, China. The ΔG_{iwi} of NOM in the water samples was also correlated to their LnK_{ATPS} ($R^2 = 0.89$, Fig. 6b). These aquatic NOM is hydrophilic in nature with ΔG_{iwi} ranging from 5.42 to 35.58 mJ m^{-2} and K_{ATPS} ranging from 0.67 to 4.33. Although equation (8) was derived using mainly reference NOM, it suggests that K_{ATPS} can be potentially used to predict the hydrophobicity of NOM (i.e., ΔG_{iwi}) in natural samples. Its prediction power was evaluated using these natural water samples. The experimentally determined ΔG_{iwi} of NOM in 20 natural water samples is in good agreement with the predicted value using equation (8) (Fig. 7), suggesting that the simple linear model based on K_{ATPS} have good prediction power for NOM hydrophobicity in natural waters. The quantification process needs only 2 mL natural water sample and is completed within 1 h, which can be further simplified during modification.

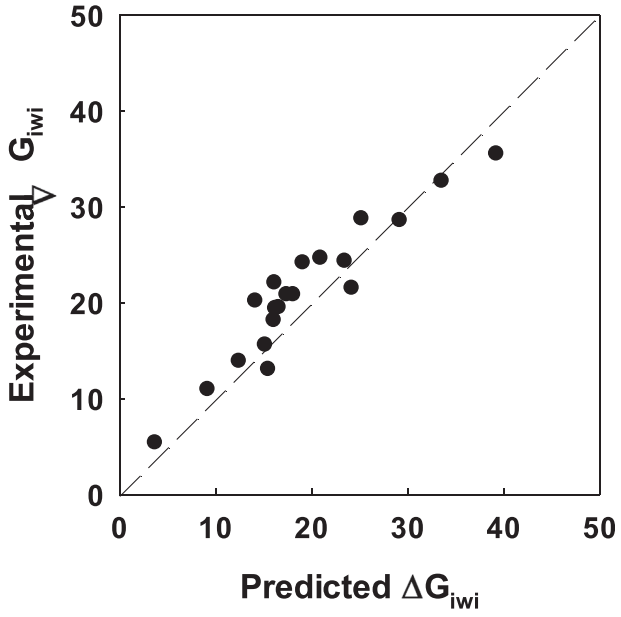

Fig. 7. Validation of the prediction power of equation (8) for quantifying NOM hydrophobicity, i.e., the free energy of interactions between NOM molecules in water (ΔG_{iwi}), using natural water samples.

4. Conclusion

This study developed an ATPS scale system for routine quantification of NOM hydrophobicity. The LnK_{ATPS} of reference NOM spanning a wide range of origins and properties correlated well with elemental, structural, and thermodynamic indices commonly used to characterize hydrophobicity, including (O + N)/C, O/C, aromatic and aliphatic carbon, and ΔG_{iwi}.

- The results indicate that K_{ATPS} can be used to quantify NOM hydrophobicity.
- A simple linear model was developed to predict NOM hydrophobicity using K_{ATPS} based on reference NOM. The model was validated using 20 natural water samples collected from rivers and lakes, which suggested good prediction power.
- Comparing with other methods, K_{ATPS} is a simple, fast, environmentally friendly, and low-cost approach to quantify hydrophobicity and facilitate characterization of NOM. This approach requires little pretreatment and small sample volume and consequently suitable for routine measurements.

- The main limitation of current method is related to the determination of K_{ATPS}. Current spectroscopic method did not account for the distribution of non-chromophores and was influenced by the fractionation of NOM in ATPS. Although the results suggest spectroscopically determined K_{ATPS} serves as good indicator for NOM hydrophobicity, more accurate quantification method is in need for K_{ATPS}.
- ATPS systems are likely to find wide applications in characterizing environmental and engineered processes involving interactions with NOM (e.g., fouling of membrane systems and formation of disinfection byproducts), which warrants further investigation.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2018.11.183.

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