

Characterizing the Bioavailability of Cationic Surfactants using Passive samplers

Yi Chen[†]✉, Steven T.J. Droge^{†,‡}, Joop L.M. Hermens[†]

[†] Institute for Risk Assessment Sciences (IRAS), Utrecht University, The Netherlands

✉ y.chen@uu.nl

[‡] Department of Analytical Environmental Chemistry, UFZ - Helmholtz Centre for Environmental Research, Leipzig, Germany

Universiteit Utrecht

Introduction

- Cationic surfactants are widely used chemicals, and trace level have been detected in sediment monitoring [1]
- Free concentrations of cationic surfactants are lower, but difficult to determine
- We optimized the ion-exchange SPME method to characterize the sorption behavior of two cationic surfactants to organic matter

Material and methods

- Purified Aldrich humic acid (PAHA) according to [2], organic carbon content ~60%
- 1-day equilibrium with PAHA (10 mg/L)
- 2-day exposure of 7- μ m polyacrylate (PA) SPME fiber in batch sorption test
- Extraction and HPLC mobile phase: methanol/ water (90/10,v/v) 0.1% TFA
- SPE extracting total dissolved concentrations (C_{aq}), using Oasis WCX column
- K_{fw} (C_f/C_{aq}) obtained in different media
- C_s calculated via mass balance
- Analyzed on LC-MS/MS

Conclusions

- The ion-exchange SPME method is suitable for determining the freely dissolved cationic surfactant concentration
- The effects of medium composition on SPME calibration supports the finding of the presence of the carboxyl groups on PA fibers [3]
- Application in sorption or toxicity tests requires SPME calibration in the test medium
- The applicable SPME concentrations for IV-16 and C12-BAC range between 0.1 μ g/L ~ 0.1 mg/L (C_{aq})
- Strong binding of cationic surfactant to PAHA; C_{free} decreased 60-99% at 6 mg/L DOC
- Sorption of cationic surfactant likely includes both ion-exchange and non-ionic interaction
- Inorganic cations compete for the sorption sites on PAHA ($Ca^{2+} > 2 Na^+$)
- Increasing pH enhances sorption to PAHA

References

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Result I:

validation of ion-exchange SPME method (Fig. 1)

Applicable SPME concentration range: $\Sigma C_f < 2$ mmol/L PA fiber (mixture cation surfactants)

CEC of PA fiber ~ 30 mmol/L PA fiber ?

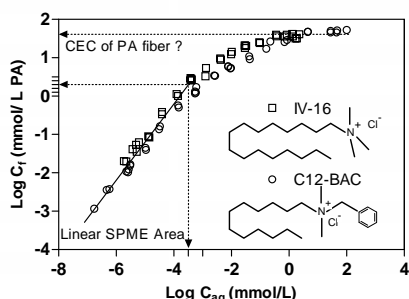


Fig. 1 SPME calibration isotherm measured in 5mM CaCl₂ (pH5.5) after 2-day exposure, arrow indicating maximum C_f (2 mmol/L PA fiber) in the linear range and possible cation exchange capacity for 7- μ m PA fiber)

Result II:

effect of solution chemistry on the SPME calibration isotherms (Fig. 2)

K_{fw} decreases with increasing concentration of inorganic cation (Fig. 2A)

Divalent cation (Ca^{2+}) is a stronger competitor than monovalent cation (Na^+) although at similar ionic strength (Fig. 2A)

Constant K_{fw} obtained above pH of 6.5, but at pH 2, K_{fw} significantly decreases a factor of 100 compared to pH 6.5 (Fig. 2B)

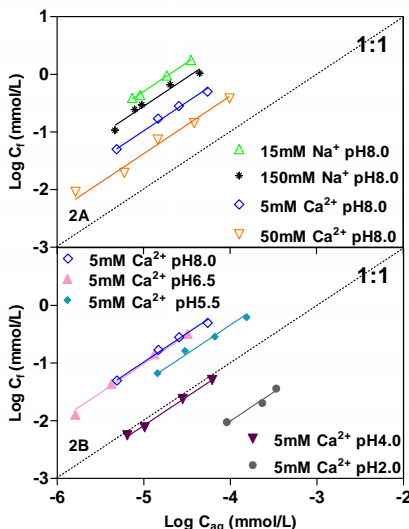


Fig. 2 2-day SPME calibration isotherms for C12-BAC influenced by medium properties: (2A) salt composition and (2B) pH. Dotted line indicates linearity.

Result III:

effect of medium composition on sorption of cationic surfactant to PAHA (Fig. 3)

Non linear sorption to PAHA, fitted with Freundlich isotherm (with Freundlich exponent, $N_f=0.82$); Given $C_{aq} = 1$ mmol/L, the calculated distribution coefficients ($\log K_d$ as L/kg) ranging from 4.4 to 5.6 (Table 1)

Table 1 Calculated $\log K_d$ (L/kg) for IV-16 and C12-BAC sorption to PAHA measured in different medium

pH	Inorganic cation	$\log K_d \pm SE$ (L/kg)	
		C12-BAC	IV-16
6.0	5 mM Ca ²⁺	4.9±0.03	5.5±0.03
	50 mM Ca ²⁺	4.4±0.04	5.2±0.04
	5 mM Na ⁺	5.4±0.04	5.6±0.04
	50 mM Na ⁺	5.4±0.06	
3.0	5 mM Na ⁺	4.5±0.05	5.2±0.06

Sorption seems to increase with surfactant alkyl chain length (Fig. 3A)

Sorption decreases with increasing Ca²⁺ (ion-exchange); little effect for Na⁺ (Fig. 3B);

Increasing pH enhances sorption (Fig. 3C)

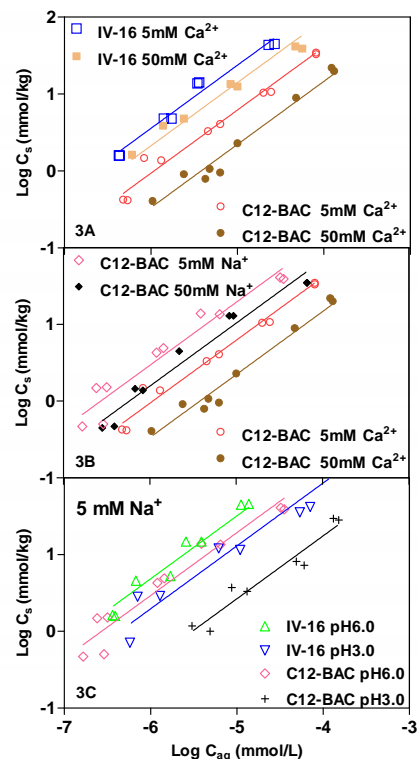


Fig. 3 Sorption of IV-16 and C12-BAC to PAHA influenced by surfactant chain length (3A), different inorganic cations (3B), and pH measured in 5mM NaCl solution (3C). Data fit with fixed nonlinearity ($N_f=0.82$).