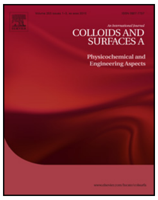
Colloids and Surfaces A: Physicochem. Eng. Aspects 520 (2017) 497–504

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa



Halogen bonding-assisted adsorption of iodoperfluoroarenes on a strong anion exchanger and its potential application in solid-phase extraction

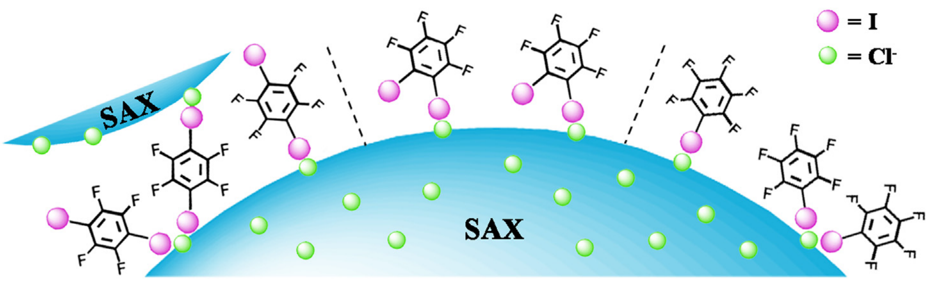
Chen Li, Lili Li, Xiaomin Yang, Wei Jun Jin*

College of Chemistry, Beijing Normal University, Beijing 100875, People's Republic of China

HIGHLIGHTS

- Halogen bonding as a new mechanism is applied into the adsorption of iodoperfluoroarenes.
- Interfacial halogen bonding can minimize solvent requirements and maximize XB strength.
- The three of iodoperfluoroarenes has different adsorption models, and this results could guide the design of XB-based self-assembly.
- Halogen bonding-assisted adsorption has a potential application in solid-phase extraction.

GRAPHICAL ABSTRACT



The adsorption of iodoperfluoroarenes by solid-liquid interfacial halogen bonding was investigated and preliminarily applied to solid-phase extraction.

ARTICLE INFO

Article history:
Received 3 August 2016
Received in revised form 25 January 2017
Accepted 3 February 2017
Available online 6 February 2017

Keywords:
Iodoperfluoroarene
Solid-liquid interface
Halogen bonding
Adsorption
SAX
Separation

ABSTRACT

The adsorption of iodoperfluoroarenes (IPFArs) by solid-liquid interfacial halogen bonding was investigated and preliminarily applied to solid-phase extraction (SPE). Based on ^{19}F NMR titration experiments, UV spectrophotometric titrations, and chemical computations, silica gel functionalized with trimethylaminopropyl chloride (SAX) groups was chosen as a strong anion-exchanging adsorbent, since the solution-phase association ability of Cl^- as halogen bond acceptor is superior to that of Br^- or I^-. Further explorations indicated that the adsorption of IPFArs is mainly driven by halogen bonding. The adsorption isotherms of 1,4-diiodotetrafluorobenzene (1,4-DITFB) and iodoperfluorobenzene (IPFB) were fitted by the Freundlich equation, while that of 1,2-diiodotetrafluorobenzene (1,2-DITFB) was fitted by the Langmuir equation. Such alternative adsorption models can meet the requirements of different self-assembly systems based on halogen bonding. In SPE applications, the adsorption efficiency of IPFArs on SAX is as follows: 1,4-DITFB $\approx$ 1,2-DITFB > IPFB, with no significant adsorption of bromoperfluoroarenes. These results indicate promising applications of halogen bonding in the separation and enrichment of IPFArs.

1. Introduction

Halogen bonding (XB) refers to an overall attractive interaction between an electrophilic region associated with a halogen atom in a molecular entity and a nucleophilic region in another or the same molecular entity [1]. This interaction exhibits high strength in many cases, particularly in nonpolar environments, as well as a high

---

* Corresponding author.
E-mail address: wjjin@bnu.edu.cn (W.J. Jin).

http://dx.doi.org/10.1016/j.colsurfa.2017.02.016
0927-7757/

Nomenclature

Abbreviations

SAX	Silica gel functionalized with trimethylaminopropyl chloride
SPE	Solid-phase extraction
XB	Halogen bonding
HPBs	Halogenated perfluorinated benzenes
IPFArs	Iodoperfluoroarenes
BrPFArs	Bromoperfluoroarenes
1,4-DITFB	1,4-diiodotetrafluorobenzene
IPFB	Iodoperfluorobenzene
1,2-DITFB	1,2-diiodotetrafluorobenzene
THF	Tetrahydrofuran
EAC	Ethyl acetate
D–R	Dubinin–Radushkevich
ΔE	The interaction energy
c_0	The initial concentrations (mmol L^{-1})
c_a	The effluent concentrations (mmol L^{-1})
A_r	The initial absorbance of the eluent
A_{r0}	The elution absorbance of the eluent
K_a	Association constants
ΔG	The Gibbs energy changes
E	The mean free energy
R^2	The value of linear correlation
q_m	The adsorption capacity

preference for directionality [2]. In addition, the XB strength can be tuned by single-atom mutation in the order I > Br > Cl [3]. These features constitute the basis of XB application in anion recognition and transport, construction of interlocked structures using anions as templates [4], organocatalysis [5], crystal engineering [6], etc.

Adsorption at the solid-liquid interface based on hydrogen bonding [7,8], electrostatic forces [9,10], complexation [11,12], multiple interactions[13], etc. has been extensively studied. However, XB received limited attention as a driving force for adsorption. Actually, due to the higher specificity of XB compared to other non-covalent interactions, XB-based adsorption can achieve separation and enrichment of the environmental pollutants with strong halogen-bonding abilities. Yan et al. [14] have successfully applied halogen bonding as a new adsorption mechanism in the solid-phase extraction of iodoperfluoroarenes (IPFArs). In the practical application, the choice of solvent is very important. Polar solvents can weaken XB due to the competition between the solvent effect and halogen bonding. In some cases, a slight decrease of solvent polarity can significantly strengthen halogen bonding [15,16]. However, insolubility of XB donors or acceptors in some apolar solvents narrows the choice of the latter for recognition, self-assembly, etc. Such problems can be solved by interfacial halogen bonding, which can minimize solvent requirements and maximize XB strength. So, the research on XB-assisted adsorption based on XB may open another door for optimizing the method of detection based on XB, such as anion recognition. Moreover, research on the nature of XB-based adsorption models can guide the design of XB-based self-assembly [17], which attracts much interest in the field of materials science.

Perfluorinated compounds (PFCs) have been recognized as emerging global pollutants due to their risk of bioaccumulation [18]. Iodoperfluoroarenes (IPFArs) as potential environmental pollutants still have not invoked special interest to detect them. In this case, three kinds of IPFArs, 1,4-diiodotetrafluorobenzene (1,4-DITFB), 1,2-diiodotetrafluorobenzene (1,2-DITFB), and iodoperfluorobenzene (IPFB) which are strong XB donors were chosen as adsorbates. Their adsorption driven by solid-liquid interfacial halogen bonding was designed, and the corresponding kinetic and thermodynamic behavior was discussed. The halogen bonding of IPFArs with different halide anions (Cl^-, Br^-, and I^-) in solution was investigated to determine the most suitable XB acceptor in the adsorbent. ^{19}F NMR titration experiments, UV–vis absorption spectra, and chemical computations indicate that Cl^- is a superior XB acceptor (compared to Br^- or I^-) for forming 1:1 complexes with IPFArs in solution. Regarding the choice of solvent, experimental results prove that using apolar *n*-hexane can minimize the solvent effect in the adsorption process. Thus, the characteristics of adsorption of these IPFArs from *n*-hexane onto the surface of a strong anion exchanger (silica gel modified with trimethylaminopropyl chloride (SAX) groups) were further explored. Prominent red shifts of characteristic Raman spectra indicate that XB is the main driving force for such interfacial adsorption. According to the simulated adsorption isotherms, the three IPFArs possess two kinds of adsorption models with different maximal adsorption capacities, providing a theoretical basis for the selective adsorption of halogen bonding donor IPFArs. Finally, a solid phase extraction (SPE) method using XB-assisted adsorption was proposed. Bromoperfluoroarenes or other weaker XB donors can not be adsorbed by SAX, which further proves that selectively adsorption of IPFArs on SAX by forming XB complexes should be significant in the separation of IPFArs [19].

2. Experimental section

2.1. Materials

1,4-Diiodotetrafluorobenzene ($C_6F_4I_2$), 1,2-diiodotetrafluorobenzene ($C_6F_4I_2$), and iodoperfluorobenzene (C_6F_5I) were purchased from Sigma-Aldrich. Tetra-*n*-butylammonium chloride ($Bu_4N^+Cl^-$), tetra-*n*-butylammonium bromide ($Bu_4N^+Br^-$), and tetra-*n*-butylammonium iodide ($Bu_4N^+I^-$) were purchased from TCI Co. (Tokyo, Japan). Acetonitrile (CH_3CN), methanol (CH_3OH), tetrahydrofuran (THF), ethyl acetate (EAC), dichloromethane (CH_2Cl_2), and *n*-hexane were purchased from Beijing Chemical Reagent Plant (analytical grade, +99.0%). Trifluoroacetic acid was purchased from Acros Organics. Bond Elut-Si silica gel (40 μm) was purchased from Agela (Tianjin, China). BONDESIL-SAX (40 μm, 1.85 mequiv g^{-1} anion exchange capacity) was purchased from Agilent Co. (CA, USA). Cleanert-SAX (40 μm, 0.3 mequiv g^{-1} ion exchange capacity) was purchased from Agela (Tianjin, China). Bromide and iodide anion exchangers were not available commercially. Acetonitrile (99.5%) was dried using 3 Å molecular sieves prior to being used for spectral measurements.

2.2. Computational methods

All calculations were carried out using the Gaussian09 quantum chemistry package [20] and the M06-2X density functional [21]. The 6-311++G(d,p) basis set was used to describe C, H, F, Cl, and Br atoms, and the I atom was described by 6-311++G(d,p)/LANL2DZdp ECP. The interaction energy (ΔE) of each complex was calculated as the difference between the energy of the complex and the sum of total energies of the monomers, $\Delta E_{total} = E_{AB} - (E_A + E_B)$. The basis set superposition error (BSSE) was estimated using the counterpoise (CP) method of Boys-Bernardi. Fully optimized calculations in solution were performed using the standard polarizable continuum model (PCM).

2.3. Spectral measurements

UV–vis absorption spectra were recorded on a TU-1901 spectrophotometer (Beijing Purkinje General Instrument Co., Beijing,