

pubs.acs.org/NanoLett

Thermodynamic Profiles at the Solvated Inorganic–Organic Interface: The Case of Gold–Thiolate Monolayers

Venkataramanan Ravi, Jason M. Binz, and Robert M. Rioux

Department of Chemical Engineering, The Pennsylvania State University, University Park, Pennsylvania 16802, United States



Nano Lett. 2013 13 4442-4448 Ananya Baksi

12/04/2014

Introduction

✓ The study of surface and interfacial properties at an organic-nanoparticle interface through the binding of suitable ligands is vital to obtain desired functionalities for a wide range of applications in nanotechnology and nanobiotechnology.

✓ The kinetic and thermodynamic contributions to the adsorption/self-assembly of organic molecules enables an assessment of the relationships that exist between the head group interactions with the metal surface and the tail group interactions with adjacent adsorbates.

✓ The complexity associated with understanding these interactions arises because several of them occur simultaneously- hydrogen bonding, van der Waals interactions, solute-solvent interactions, and solvent reorganization-which influence the structural details of the final organic-inorganic interface and the measured thermodynamics.

✓ These interactions exhibit thermodynamic behaviors that vary over a wide range of energy with both parallel and series kinetics that span several timescales. From an experimental standpoint, these interactions are not well-quantified in solvated systems since it is difficult to interrogate interfaces buried by solvent. Formation of Monolayers by the Coadsorption of Thiols on Gold: Variation in the Head Group, Tail Group, and Solvent¹

Colin D. Bain,² Joe Evall, and George M. Whitesides*

Direct Measurement of the Adsorption Kinetics of Alkanethiolate Self-Assembled Monolayers on a Microcrystalline Gold Surface

D. S. Karpovich and G. J. Blanchard*

Quantitating the Balance between Enthalpic and Entropic Forces in Alkanethiol/Gold Monolayer Self Assembly

H. M. Schessler, D. S. Karpovich, and G. J. Blanchard*

Sticking Probabilities in Adsorption of Alkanethiols from Liquid Ethanol Solution onto Gold

Linda S. Jung and Charles. T. Campbell*

Introduction

✓ Self-assembled organic monolayers (SAMs) represent the quintessential nanoscale organic–inorganic interface because they provide an organic platform of controllable molecular thickness able to anchor different chemical species by a multitude of interactions.

✓ ITC can be used to measure the equilibrium adsorption constant, enthalpy of adsorption, and adsorption stoichiometry in a single experiment. This allows for a full thermodynamic description of thiol adsorption on a solvated Au NP, which is advantageous over an indirect approach, like van't Hoff analysis, which requires multiple experiments conducted at various temperatures.

✓ Here they report the influence of alkyl chain length, temperature, particle size, and solvent contributions on the thermodynamic description of carboxylic acid terminated thiol adsorption on Au NPs.

Nano ITC



SPECIFICATIONS

	Standard Volume	Low Volume
Temperature Range	2 to 80°C	2 to 80°C
Temperature Stability	0.0002°C @25°C	0.0002°C @25°C
Minimum Detectable Heat	0.1 µJ	0.05 μJ
Maximum Detectable Heat	5,000 μJ	3,000 μJ
Baseline Stability	0.02 μW/hr	0.02 μW/hr
Noise Level	0.0025 μWatt	0.0014 μWatt
Response Time	13 Seconds	11 Seconds
Cell Volume	1.0 mL	190 µL
Cell Configuration	Fixed-in-place, Cylindrical	Fixed-in-place, Cylindrical
Cell Material	24K Gold or Hastelloy	24K Gold
Injection Syringe Volumes	100 µL and 250 µL	50 μL



The Nano IIC can easily detect the most subtle heat flow events, and the ultra-short time constant of the power compensation cell ensures the highest peak resolution.

Materials and characterization



TEM image of different nanoparticles showing size 5.4, 9.5 and 19.4 nm

According to the statistics of surface atoms for a cuboctahedral particle developed from van Hardeveld and Hartog, we estimated the number of Au surface atoms located on (111) and (100) facets for each NP size as follows:

Au NP diameter (nm)	Total number of Au atoms	Au (111) surface atoms	Au (100) surface atoms	Au corner and edge atoms	% Au (111) surface atoms
5	3860	848	210	120	71.9
10	30896	3440	858	264	75.4
20	247168	12680	3168	528	77.4

$$R_{NP} = R_{atom} \times N_t^{1/3}$$

$$N_{S} = \frac{\text{Surface area of nanoparticle}}{\text{Cross Sectional Area of individual atom}} = \frac{4\pi (R_{NP})^{2}}{\pi (R_{atom})^{2}} = 4 \times N_{t}^{2/3}$$

Experimental parameters

Thiol	NP size	$\left[Au_{s}\right]\left(mM\right)$	[Ligand]	$V_{ m inj}$	$N_{ m inj}$	t _{inj} (s)
C ₂ -TGA	5.4	0.08	0.5	6	16	800
2	9.5	0.04	0.2	6	16	800
· · · ·	5.4	0.08	0.5	6	16	800
C ₃ -MPA	9.5	0.04	0.3	6	16	800
	19.4	0.02	0.15	5	20	1000
C ₆ -MHA	5.4	0.08	0.4	6	16	800
	9.5	0.04	0.2	5	19	800
	19.4	0.02	0.1	6	16	800

Experimental conditions for ITC experiments on different nanoparticle sizes. For each experiment listed, the gold nanoparticle and thiol concentrations are provided, along with the volume of each injection (Vinj), the total number of injections (Ninj), and the duration of each injection (tinj) which refers to the amount of time that elapses after an injection in order to allow the baseline to equilibrate.



Real-time ITC thermograms for C2-TGA at pH (A) 4, (B) 6.1, and (C) 7 binding to 5.4 ± 0.7 nm Au NPs at 298.15 K with D, E, and F as the respective integrated heat data with fitted models. D is fit using multiple-sites model, and E is fit using both multiple-sites and independent models, while F is fit using an independent model. "Q" refers to the thermal compensation of the calorimeter to keep the sample at a constant temperature (positive peaks are exothermic). Each peak corresponds to a single injection of C2-TGA solution into the nanoparticle suspension.



Real-time ITC thermograms at pH 6.1 for (A) C3-MPA and (B) C6-MHA binding to 5.4 ± 0.7 nm Au NPs at 298.15 K with C and D as the respective integrated heat data with an independent model fit.



Differential enthalpy of adsorption (Δ H) with coverage for (•) C2-TGA, (**■**) C3-MPA, and (•) C6-MHA on 5.4 ± 0.7 nm Au nanoparticles at 298.15 K.

Thiol	T(K)	$K(M^{-1})$	ΔG^a (kcal/mol)	ΔH^b (kcal/mol)	$T\Delta S^a$ (kcal/mol)	n	$\Delta C_p \text{ (kcal/mol·K)}$
C2-TGA	283.15	$(1.4 \pm 1.2) \times 10^{7}$	-9.3 ± 0.8	-23.6 ± 2.2	-14.4 ± 1.4	0.26 ± 0.02	0.25 ± 0.07
	293.15	$(1.3 \pm 0.9) \times 10^7$	-9.5 ± 0.9	-20.5 ± 1.2	-10.9 ± 0.9	0.33 ± 0.02	
	298.15	$(5.1 \pm 1.3) \times 10^{6}$	-9.1 ± 1.1	-20.0 ± 1.3	-10.9 ± 1.2	0.33 ± 0.01	
	303.15	$(4.2 \pm 1.1) \times 10^{6}$	-9.2 ± 0.9	-18.4 ± 1.1	-9.2 ± 1.1	0.34 ± 0.01	
C3-MPA	283.15	$(8.5 \pm 0.7) \times 10^{6}$	-8.9 ± 0.7	-22.8 ± 0.2	-13.9 ± 0.7	0.27 ± 0.02	0.3 ± 0.04
	293.15	$(5.7 \pm 0.6) \times 10^{6}$	-9.0 ± 0.2	-21.2 ± 0.7	-12.2 ± 0.2	0.30 ± 0.03	
	298.15	$(3.3 \pm 0.5) \times 10^{6}$	-8.9 ± 0.4	-20.3 ± 1.1	-11.4 ± 0.4	0.37 ± 0.01	
	303.15	$(3.1 \pm 0.4) \times 10^{6}$	-9.0 ± 0.5	-13.7 ± 0.6	-4.7 ± 0.5	0.30 ± 0.01	
C6-MHA	283.15	$(8.9 \pm 0.1) \times 10^{6}$	-9.0 ± 0.1	-34.4 ± 1.2	-25.4 ± 0.1	0.20 ± 0.02	0.4 ± 0.02
	293.15	$(5.9 \pm 0.7) \times 10^{6}$	-9.1 ± 0.6	-30.6 ± 0.5	-21.5 ± 0.6	0.16 ± 0.02	
	298.15	$(2.7 \pm 0.4) \times 10^{6}$	-8.8 ± 0.2	-28.6 ± 0.2	-19.8 ± 0.2	0.20 ± 0.01	
	303.15	$(1.2 \pm 0.6) \times 10^{6}$	-8.4 ± 0.2	-26.8 ± 0.7	-18.4 ± 0.2	0.24 ± 0.01	
				-			

Temperature Dependence of the Adsorption Constant (K), Gibbs Free Energy of Adsorption (ΔG), Enthalpy of Adsorption (ΔH), Entropy of Adsorption ($T\Delta S$), and Molar Heat Capacity (ΔCp) of C2-TGA, C3-MPA, and C6-MHA on 5.4 ±0.7 nm Au Nanoparticles at a pH of 6.1

Thiol	Au NP (nm)	$K(M^{-1})$	ΔG (kcal/mol)	$\Delta H (\text{kcal/mol})$	$T\Delta S$ (kcal/mol)	n
C2-TGA	5.4 ± 0.7	$(5.1 \pm 1.3) \times 10^{6}$	-9.1 ± 1.1	-20.0 ± 1.3	-10.9 ± 1.2	0.33 ± 0.01
	9.5 ± 0.6	$(3.9 \pm 1.5) \times 10^{6}$	-9.0 ± 1.3	-18.2 ± 1.6	-9.2 ± 1.4	0.27 ± 0.02
C ₃ -MPA	5.4 ± 0.7	$(3.3 \pm 0.5) \times 10^{6}$	-8.9 ± 0.4	-20.3 ± 1.1	-11.4 ± 0.4	0.37 ± 0.01
	9.5 ± 0.6	$(8.4 \pm 0.3) \times 10^{6}$	-9.4 ± 0.5	-19.7 ± 0.1	-10.3 ± 0.5	0.32 ± 0.01
	19.4 ± 1.1	$(4.5 \pm 0.9) \times 10^{6}$	-9.1 ± 0.1	-17.3 ± 0.3	-8.2 ± 0.1	0.30 ± 0.02
C ₆ -MHA	5.4 ± 0.7	$(2.7 \pm 0.4) \times 10^{6}$	-8.8 ± 0.2	-28.6 ± 0.2	-19.8 ± 0.2	0.20 ± 0.01
	9.5 ± 0.6	$(9.4 \pm 0.7) \times 10^{6}$	-9.5 ± 0.5	-24.7 ± 0.3	-15.2 ± 0.4	0.27 ± 0.01
	19.4 ± 1.1	$(8.8 \pm 0.8) \times 10^{6}$	-9.4 ± 0.4	-17.9 ± 0.3	-8.5 ± 0.4	0.22 ± 0.01

Gold Nanoparticle Size Dependence on the Adsorption Constant (K), Gibbs Free Energy of Adsorption (ΔG), Enthalpy of Adsorption (ΔH), and the Entropy of Adsorption ($T\Delta S$) of C2-TGA, C3-MPA, and C6-MHA at 298.15 K

рН	$\begin{matrix} K_1 \\ K_2 \\ (M^{-1}) \end{matrix}$	ΔH_1 ΔH_2 (kcal/mol) ^b	$\frac{T\Delta S_1}{T\Delta S_2}$ (kcal/mol) ^a	n_1 n_2
4.0	$(6.2 \pm 0.7) \times 10^{5}$	-11.4 ± 0.7	-3.5 ± 0.4	0.28 ± 0.01
4.0	$(4.8 \pm 0.5) \times 10^{8}$	-6.5 ± 0.5	5.3 ± 0.5	0.19 ± 0.01
6.1	$(6.4 \pm 0.6) \times 10^{6}$	$\textbf{-29.8} \pm 0.8$	-20.5 ± 0.6	0.29 ± 0.02
	$(1.1 \pm 0.4) \times 10^{6}$	-10.3 ± 0.5	-2.1 ± 0.5	0.27 ± 0.02
7.0	$(7.2\pm0.6)\times10^6$	-11.2 ± 0.6	-1.9 ± 0.5	0.4 ± 0.02
/.0				

pH dependence of the association constant (K), Gibbs free energy of adsorption (ΔG), enthalpy of adsorption (ΔH), and entropy of adsorption ($T\Delta S$) of C2-TGA on 5.4 ± 0.7 nm Au nanoparticles (0.08 mM Aus) at 298.15 K.



Thermogravimetric analysis data for (A) 5.4 ± 0.7 nm and (B) 9.5 ± 0.6 nm Au NPs saturated with C3-MPA.



Thiol	ΔH_{solv}
	(cal/mol)
C ₂ -TGA	0.86
C ₃ -MPA	1.17
C ₆ -MHA	0.55

Experimental compensation plot for the enthalpy and entropy of adsorption for C6-MHA adsorption on 5.4 ± 0.7 , 9.5 ± 0.6 , and 19.4 ± 1.1 nm Au NPs at 298.15 K.

Solution calorimetry data for dissolution of pure C2-TGA, C3-MPA, and C6-MHA at 298.15 K in water.

✓ They have provided a detailed analysis of the thermodynamic profiles at a solvated organic-inorganic interface by considering the binding of various carboxylic acid-terminated alkanethiols to Au NP surfaces.

✓ For all three thiols tested, the magnitude of ∆H was found to linearly increase with increasing alkyl chain length, decreasing temperature, and decreasing Au NP size. Thiol-NP interactions are enthalpy-driven and are accompanied by an unfavorable entropic contribution mainly associated with the reduced translational (2D versus 3D), reduced alkyl chain rotation, and hindered trans/gauche interconversion.

 \checkmark ITC studies on larger nanocrystals with well-defined surfaces (with one specific facet) and a mixture of surfaces can help one understand how molecular or polymeric entities influence the faceting of nanoparticles.

 \checkmark The use of complementary calorimetric techniques opens possibilities to study a broad class of hybrid organic–inorganic composites to give insight into bond formation and ordering. Future studies will also include the construction of a Born–Haber cycle to deconvolute the intrinsic binding thermodynamics from the thermodynamic contributions of the solvent to the observed values, and also to quantify the effect different solvents have on binding equilibria.

Future Perspective

Sample	Sample Conc. (mM)	GSH (mM)	Ν	K*105 (M-1)	ΔH*103 (cal/mol)	ΔS (cal/degre e/mol)	Т (К)	ΔG *103 (cal/mol)
AgNO3	1	10	0.80	2.11	-16.8	-32.10	303	-7.07
Ag32(SG)1 9	1	10	0.60	1.88	-16.7	-31.10	303	-7.28
AgNP@SG	1	10	0.60	4.73	-04.0	12.70	303	-7.86

Try to see the interaction while ligand exchange
 Can be tried for metal ion interaction with clusters

Thank