Electronic Supporting Information

Influence of Immobilized Cations on the Thermodynamic Signature of Hydrophobic Interactions at Chemically Heterogeneous Surfaces

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Surfaces	**Temperature (K)**	**Number of test events / Number of samples (n / N)**					
		Aqueous TEA pH 3.5	**Aqueous TEA pH 7.0**	**Aqueous TEA pH 10.5**	**60 vol% MeOH pH 3.5**	**60 vol% MeOH pH 7.0**	**60 vol% MeOH pH 10.5**
Methyl	**298**	1,048 / 5	1,924 / 7	1262 / 5	1,054 / 5	1,154 / 4	998 / 4
	308	1,061 / 5	1,966 / 7	1255 / 5	1,058 / 5	1,157 / 4	1,004 / 4
	318	1,503 / 5	1,976 / 7	1276 / 5	1,001 / 5	1,139 / 4	1,006 / 4
	328	976 / 5	1,961 / 7	1274 / 5	1,002 / 5	1,136 / 4	1,019 / 4
100% Am	**298**	1,006 / 5	1,267 / 5	1305 / 5	1,006 / 5	1,503 / 6	1,256 / 5
	308	1,014 / 5	1,259 / 5	1305 / 5	1,008 / 5	1,424 / 6	1,258 / 5
	318	1,024 / 5	1,256 / 5	1307 / 5	1,010 / 5	1,405 / 6	1,291 / 5
	328	1,010 / 5	1,257 / 5	1309 / 5	1,013 / 5	1,392 / 6	1,262 / 5
100% Gdm	**298**	1,011 / 5	1,406 / 5	1507 / 6	1,206 / 6	1,009 / 4	953 / 4
	308	1,030 / 5	1,405 / 5	1511 / 6	1,205 / 6	1,004 / 4	953 / 4
	318	1,006 / 5	1,433 / 5	1516 / 6	1,204 / 6	1,041 / 4	967 / 4
	328	1,010 / 5	1,417 / 5	1518 / 6	1,087 / 6	1,005 / 4	965 / 4
40% Am	**298**	1,420 / 7	1,515 / 6	1505 / 6	1,614 / 8	2,109 / 8	1,341 / 5
	308	1,408 / 7	1,507 / 6	1517 / 6	1,611 / 8	2,128 / 8	1,320 / 5
	318	1,407 / 7	1,522 / 6	1502 / 6	1,633 / 8	2,115 / 8	1,253 / 5
	328	1,352 / 7	1,507 / 6	1514 / 6	1,548 / 8	2,102 / 8	1,304 / 5
40% Gdm	**298**	1,605 / 8	1,205 / 5	1203 / 5	1,186 / 6	1,349 / 6	1,822 / 8
	308	1,620 / 8	1,994 / 5	1205 / 5	1,197 / 6	1,320 / 6	1,748 / 8
	318	1,569 / 8	1,204 / 5	1225 / 5	1,163 / 6	1,317 / 6	1,753 / 8
	328	1,535 / 8	1,205 / 5	1211 / 5	1,107 / 6	1,203 / 6	1,719 / 8

Table S1. Statistical information - Number of independent samples (N) and force measurements (n) with pure methyl surface (“Methyl”), pure amine surface (“100% Am”), pure guanidine surface (“100% Gdm”), mixed amine/methyl surface (“40% Am”) and mixed guanidine/methyl surface (“40% Gdm”).

Scenario	Initial state (in 60 vol% MeOH)	Transfer	Final state (in aqueous TEA)
S1	Associated	Associated	Associated
S2	Dissociated	Dissociated	Dissociated
S3	Associated	Associated	Dissociated
S4	Dissociated	Dissociated	Associated

Table S2. Four possible scenarios for the association/dissociation of counter ions with protonated amine groups. See Section S4.

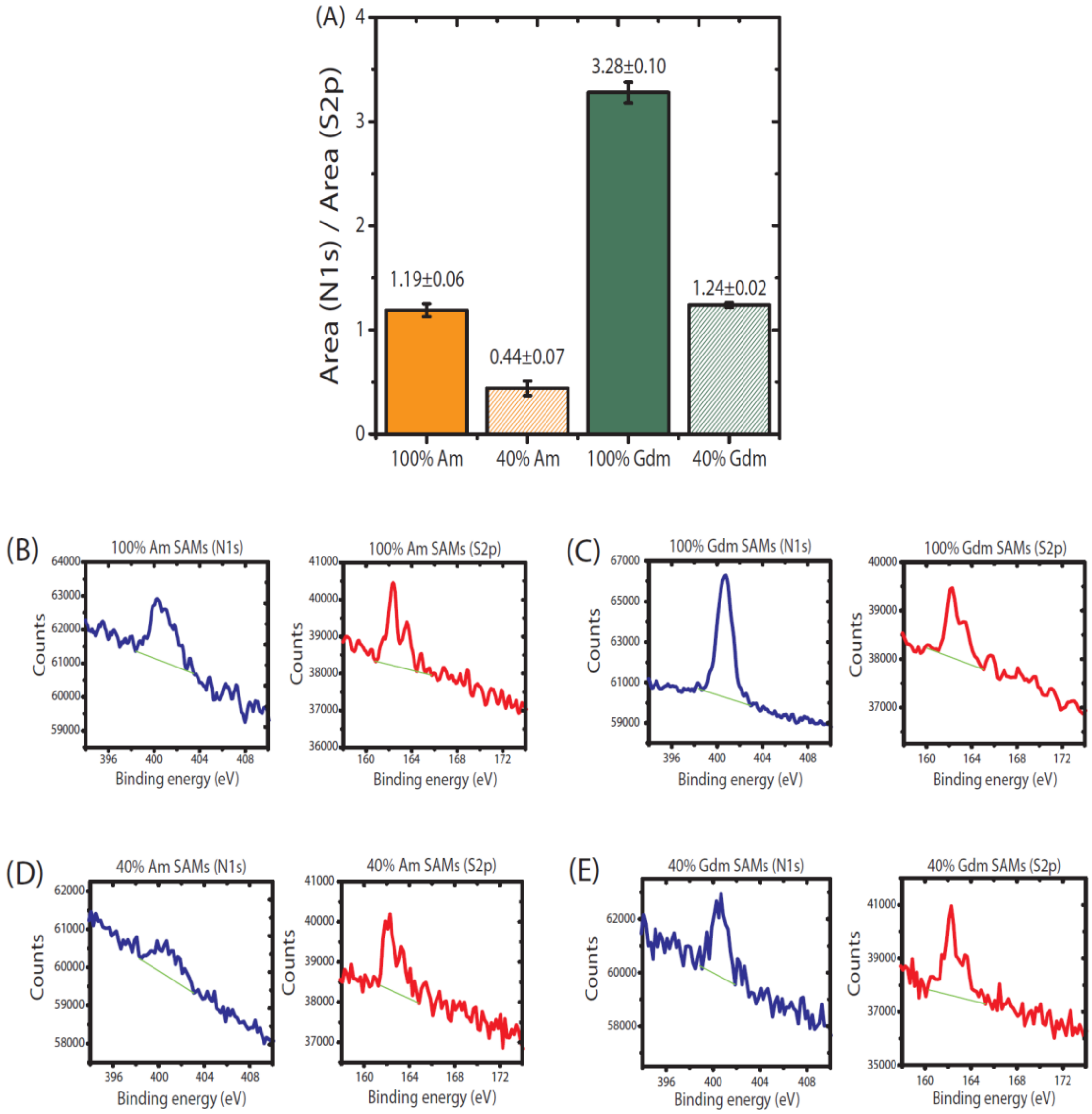


Figure S1. Characterization of the atomic composition of pure- and mixed-component amine or guanidine SAMs. (A) Ratio of nitrogen (N1s) to sulfur signal (S2p), obtained by X-ray photoelectron spectroscopy (XPS), was plotted for pure amine ("100% Am", filled) and mixed amine/methyl surfaces ("40% Am", dashed) in orange, and for pure guanidine ("100% Gdm", filled) and mixed guanidine/methyl surfaces ("40% Gdm", dashed) in green. (B-E) Nitrogen (N1s, blue) and sulfur (S2p, red) XPS signals for pure amine (B), pure guanidine (C), mixed amine/methyl (D), and mixed guanidine/methyl (E) monolayer surfaces formed on gold surfaces.

Calibration of the spring constant of AFM cantilevers.

We calibrated the spring constants of the AFM cantilevers used in our force measurements (nominal spring constant: 0.1 N m^{-1}) using Sader's method on a PCM-90 Spring Constant Calibration Module (Novascan Technologies, Ames, IA)[1,2]. Figure S3 shows the calibrated spring constants of eleven independent AFM probes after gold deposition (dashed) in comparison with the nominal spring constant (0.1 N m^{-1}, filled). The average value of the calibrated spring constant obtained using eleven independent AFM probes is 0.3395 ± 0.007 N m^{-1}.

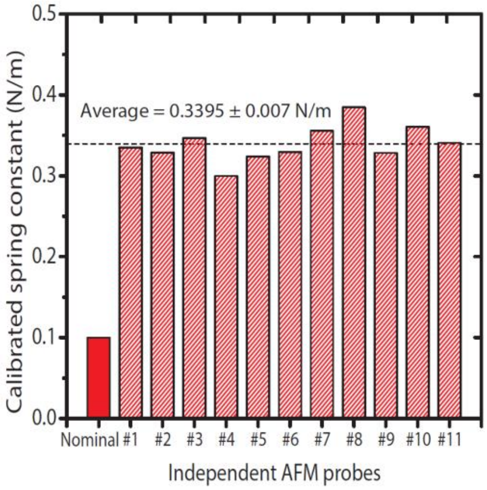


Figure S2. Calibrated spring constants of AFM cantilevers after gold deposition (nominal spring constant: 0.1 N m^{-1}). The eleven independent AFM probes were randomly selected.

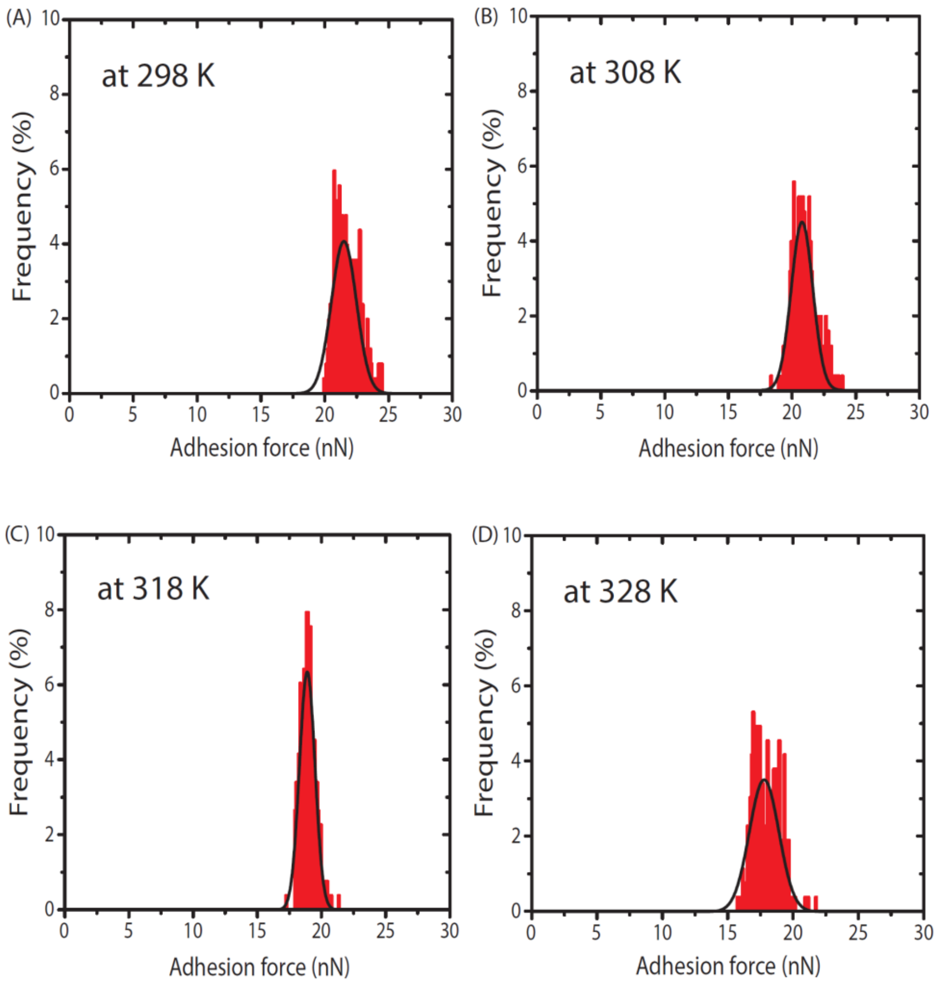


Figure S3. Representative histograms of adhesive forces measured between 1-dodecanethiol SAMs (AFM tip) and 1-decanethiol SAMs (substrate) in 10 mM aqueous TEA (pH 7.0) at 298 K (A), 308 K (B), 318 K (C), and 328 K (D), respectively.

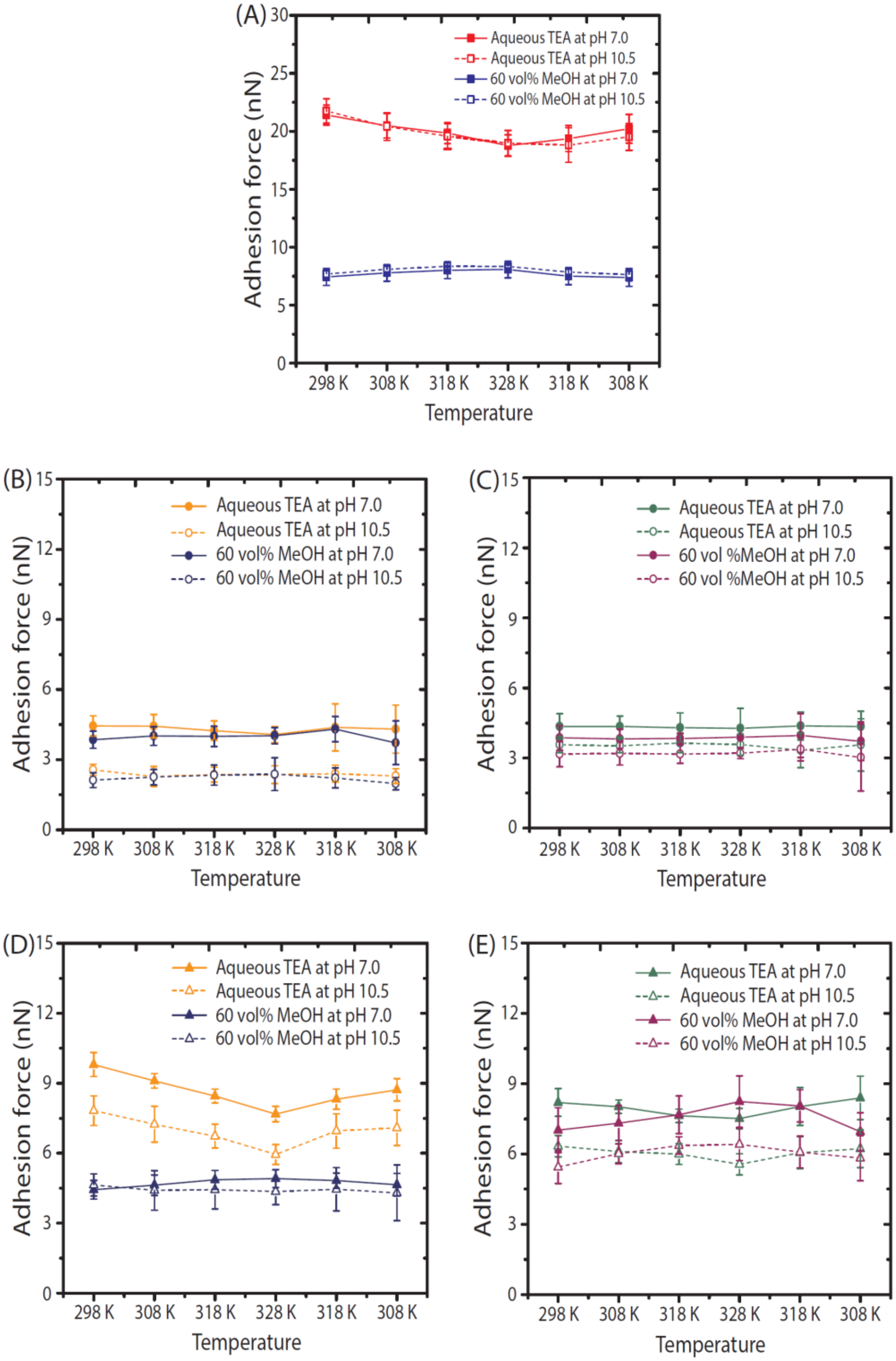
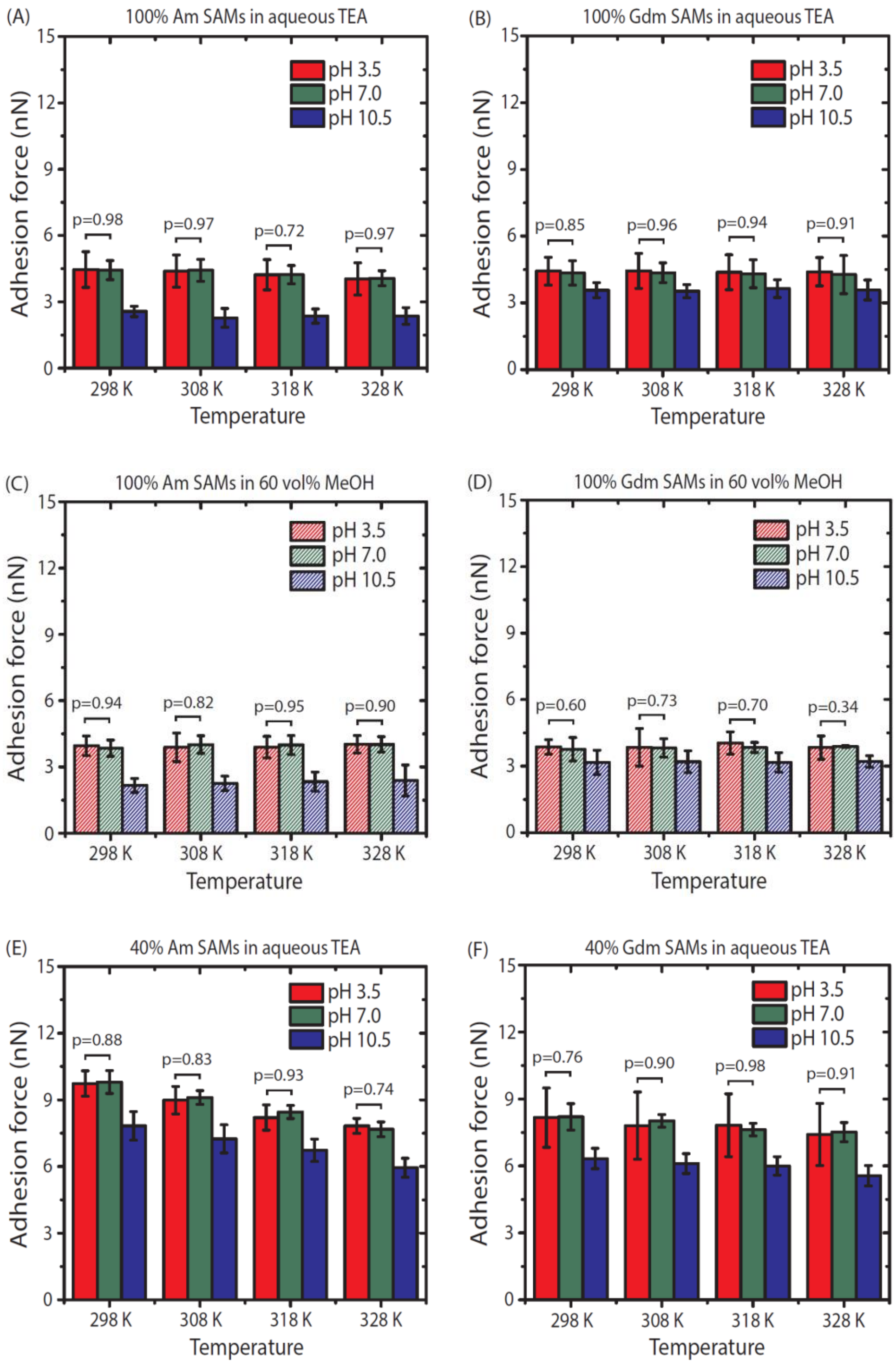


Figure S4. (A) Reversibility of mean adhesive forces measured between methyl-terminated SAMs in aqueous TEA (red) or 60 vol% MeOH added to aqueous TEA (blue) at pH 7.0 (filled) and 10.5 (open), respectively, as a function of temperature. (B and C) Reversibility of mean adhesive forces measured between the nonpolar AFM tip and (B) pure amine or (C) pure guanidine surfaces in aqueous TEA (orange and green for pure amine and pure guanidine surfaces, respectively) or 60 vol% methanol added to aqueous TEA (navy and purple for pure amine and pure guanidine surfaces, respectively) at pH 7.0 (filled) and 10.5 (open), respectively. (D and E) Reversibility of mean adhesive forces measured as a function of temperature between a nonpolar AFM tip and (D) mixed amine/methyl or (E) mixed guanidine/methyl surfaces in aqueous TEA (orange and green for mixed amine/methyl and mixed guanidine/methyl surfaces, respectively) or 60 vol% methanol added to aqueous TEA (navy and purple for mixed amine/methyl and mixed guanidine/methyl surfaces, respectively) at pH 7.0 (filled) and 10.5 (open), respectively. The temperature was elevated from 298 K to 328 K and then decreased to 308 K in steps of 10 K. We performed multiple t-tests between mean adhesive forces measured at 308 K before and after heating to 328 K, and found that p-values for pure methyl (A) and pure- and mixed-component monolayer surfaces presenting amine or guanidine groups (B-E) are > 0.05. This result reveals that the adhesive forces measured at 308 K before and after heating up to 328 K are not statistically different at a significance level of 95 %. These results also show that i) there is no significant change in composition of 60 vol% MeOH added to aqueous TEA due to evaporation during the force measurements and ii) the monolayers are thermally stable in this temperature interval.


(A)
100% Am SAMs in aqueous TEA
(B)
100% Gdm SAMs in aqueous TEA
(C)
100% Am SAMs in 60 vol% MeOH
(D)
100% Gdm SAMs in 60 vol% MeOH
(E)
40% Am SAMs in aqueous TEA
(F)
40% Gdm SAMs in aqueous TEA
Adhesion force (nN)
0
3
6
9
12
15
298 K
308 K
318 K
328 K
Temperature
pH 3.5
pH 7.0
pH 10.5
p=0.98
p=0.97
p=0.72
p=0.97
p=0.85
p=0.96
p=0.94
p=0.91
p=0.94
p=0.82
p=0.95
p=0.90
p=0.60
p=0.73
p=0.70
p=0.34
p=0.88
p=0.83
p=0.93
p=0.74
p=0.76
p=0.90
p=0.98
p=0.91

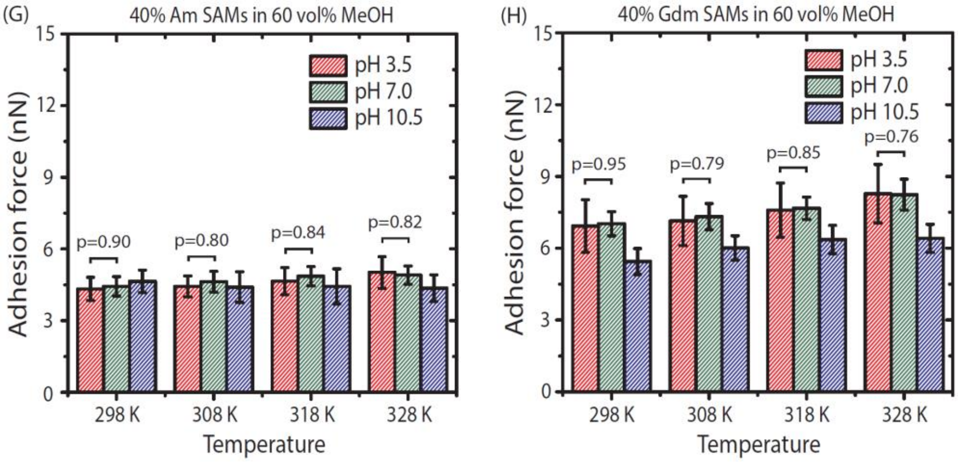


Figure S5. pH dependence of mean adhesive forces between the nonpolar AFM tip and pure- or mixed-component amine or guanidine monolayer surfaces measured in aqueous TEA (filled) or 60 vol% MeOH added to aqueous TEA (dashed). (A-D) Mean adhesive forces measured between the nonpolar AFM tip and pure amine (A and C) or pure guanidine (B and D) surfaces in aqueous TEA (A and B) or 60 vol% MeOH added to aqueous TEA (C and D) at pH 3.5 (red), 7.0 (green), and 10.5 (blue), respectively. (E-H) Mean adhesive forces measured between the nonpolar AFM tip and mixed amine/methyl (E and G) or mixed guanidine/methyl (F and H) surfaces in aqueous TEA (E and F) or 60 vol% MeOH added to aqueous TEA (G and H) at pH 3.5 (red), 7.0 (green), and 10.5 (blue), respectively. We performed multiple t-tests between mean adhesive forces measured at pH 3.5 and 7.0 to identify the charge status of immobilized amine or guanidine groups at all temperatures. We found that p-values for all pure- and mixed-component monolayer surfaces presenting amine or guanidine groups are > 0.05, revealing the mean adhesive forces measured at pH 3.5 and 7.0 to be statistically identical at a significance level of 95 % (i.e., immobilized amine and guanidine groups are fully protonated at pH ≤ 7.0).

Section S1. Evaluation of the transfer free energy of functionalized SAMs

We used Johnson-Kendall-Roberts (JKR) theory[3] to evaluate the free energy change associated with transfer of the functionalized SAMs ("s2") from aqueous TEA containing 60 vol% MeOH to aqueous TEA (i.e., transfer free energy) (See Figure 3A in the Main text). The work of adhesion ($W_{ad,M}$) between the two SAMs (s1 and s2) in the presence of medium (M) is evaluated as

$$W_{ad,M} = \gamma_{s_1-M} + \gamma_{s_2-M} - \gamma_{s_1-s_2} \quad \text{(S1)}$$

where γ_{s_1-M} and γ_{s_2-M} are the interfacial free energies of each SAM in contact with a medium after separation, respectively. $\gamma_{s_1-s_2}$ is the interfacial free energy before separation of the SAMs. The interfacial free energies were calculated as the work done in two steps of an imaginary process, as described in Figure S6 (and as described in our past study[2]) as

$$\gamma_{s_1-M} = \gamma_{s_1} + \gamma_M - W_{s_1-M} \quad \text{(S2a)}$$

$$\gamma_{s_2-M} = \gamma_{s_2} + \gamma_M - W_{s_2-M} \quad \text{(S2b)}$$

$$\gamma_{s_1-s_2} = \gamma_{s_1} + \gamma_{s_2} - W_{s_1-s_2} \quad \text{(S2c)}$$

Where each of γ_{s_1}, γ_{s_2} and γ_M quantify the work done to create infinite, planar, non-interacting half-spaces of each SAM, and medium (M) from bulk materials (reference states), respectively. $-W_{s_1-M}$ and $-W_{s_2-M}$ describe the work performed to create interfaces between each SAM and medium, respectively. The work to create interfaces between two SAMs is denoted as $-W_{s_1-s_2}$. Equation (S1) is combined with equations (S2a), (S2b), and (S2c) to arrive at the expression

$$W_{ad,M} = 2\gamma_M - W_{s_1-M} - W_{s_2-M} + W_{s_1-s_2} \quad \text{(S3)}$$

If two surfaces are identical pure methyl SAMs ($W_{s_1-s_2} = W_{CH_3-CH_3} = 2\gamma_{CH_3}, W_{s_1-M} = W_{s_2-M} = W_{CH_3-M}$), equation (S3) can be expressed as

$$W_{ad,M} = 2\left(\gamma_{CH_3} + \gamma_M - W_{CH_3-M}\right) \quad \text{(S4)}$$

where γ_{CH_3} represents the work done to create infinite, planar, non-interacting half-spaces of pure methyl SAMs. W_{CH_3-M} is the work to create interfaces between pure methyl SAMs (CH_3) and medium (M). From equation (S2a), the third term in parenthesis on the right-hand side of equation (S4) can be expressed as

$$W_{CH_3-M} = \gamma_{CH_3} + \gamma_M - \gamma_{CH_3-M} \quad \text{(S5)}$$

The equation (S5) is incorporated into equation (S4) to give the expression

$$W_{ad,M} = 2\gamma_{CH_3-M} \quad \text{(S6)}$$

The Johnson-Kendall-Roberts (JKR) theory[3] can be used to evaluate the work of adhesion between the SAMs in the presence of medium ($W_{ad,M}$) as

$$\frac{F_{ad,M}}{R} = \frac{3}{2}\pi W_{ad,M} \quad \text{(S7)}$$

where $F_{ad,M}$ is the adhesive force between the SAMs in the presence of medium (M). R is the effective radius of contacting objects ($R^{-1} = R_1^{-1} + R_2^{-1}$ where R_1 and R_2 are radii of AFM tips and substrates, respectively). Equation (S7) is combined with equation (S6) to arrive at the expression

$$\gamma_{CH_3-M} = \frac{F_{ad,CH_3-CH_3,M}}{3\pi R} \quad \text{(S8)}$$

Equation (S8) reveals that the interfacial free energy of a pure methyl SAM in contact with medium (γ_{CH_3-M}) can be determined by the measurement of adhesive forces between a pair of pure methyl SAMs ($F_{ad,CH_3-CH_3,M}$). The interfacial free energy of a pure methyl SAM in aqueous TEA (γ_{CH_3-TEA}) and aqueous TEA containing 60 vol% MeOH ($\gamma_{CH_3-60\%MeOH}$) can be expressed as

$$\gamma_{CH_3-TEA} = \frac{F_{ad,CH_3-CH_3,TEA}}{3\pi R} \quad \text{(S9a)}$$

$$\gamma_{CH_3-60\%MeOH} = \frac{F_{ad,CH_3-CH_3,60\%MeOH}}{3\pi R} \quad \text{(S9b)}$$

where $F_{ad,CH_3-CH_3,TEA}$ and $F_{ad,CH_3-CH_3,60\%MeOH}$ are the adhesive forces measured between a pair of pure methyl SAMs in aqueous TEA or aqueous TEA containing 60 vol% MeOH, respectively. Correspondingly, the transfer free energy of a pure methyl SAM ($\Delta G_{tr,CH_3}$) can be evaluated as

$$\Delta G_{tr,CH_3} = \gamma_{CH_3-TEA} - \gamma_{CH_3-60\%MeOH} = \frac{1}{3\pi R}\left(F_{ad,CH_3-CH_3,TEA} - F_{ad,CH_3-CH_3,60\%MeOH}\right) \quad \text{(S10)}$$

Additionally, equation (S10) can be decoupled into enthalpic ($\Delta H_{tr,CH_3}$) and entropic ($T\Delta S_{tr,CH_3}$) contributions at temperature (T) as

$$\Delta G_{tr,CH_3} = \Delta H_{tr,CH_3} - T\Delta S_{tr,CH_3} \quad \text{(S11)}$$

The transfer entropy of a pure methyl SAM ($\Delta S_{tr,CH_3}$) can be evaluated by taking the derivative of transfer free energy with respect to temperature at constant pressure (p) as

$$\Delta S_{tr,CH_3} = -\left(\frac{\partial \Delta G_{tr,CH_3}}{\partial T}\right)_p = -\frac{1}{3\pi R}\left(\frac{\partial\left(F_{ad,CH_3-CH_3,TEA} - F_{ad,CH_3-CH_3,60\%MeOH}\right)}{\partial T}\right)_p \quad \text{(S12)}$$

Calculation of transfer free energy of a pure methyl SAM enables evaluation of the transfer free energy of the functionalized SAMs as follows. From equation (S3), the work of adhesion between a pure methyl SAM formed on the AFM tip and a functionalized SAM (e.g., pure- and mixed-component amine or guanidine SAMs) formed on a substrate in aqueous TEA ($W_{ad,CH_3-\text{func},TEA}$) or aqueous TEA containing 60 vol% methanol ($W_{ad,CH_3-\text{func},60\%MeOH}$) can be expressed as

$$W_{ad,CH_3-\text{func},TEA} = 2\gamma_{TEA} - W_{CH_3-TEA} - W_{func-TEA} + W_{CH_3-\text{func}} \quad \text{(S13a)}$$

$$W_{ad,CH_3-\text{func},60\%MeOH}$$

$$= 2\gamma_{60\%MeOH} - W_{CH_3-60\%MeOH} - W_{func-60\%MeOH} + W_{CH_3-\text{func}} \quad \text{(S13b)}$$

The difference between the work of adhesion before and after addition of 60 vol% MeOH into aqueous TEA corresponds to the total transfer free energy ($\Delta G_{tr,total}$). After subtraction and rearrangement, the following expression can be obtained

$$\Delta G_{tr,total} = W_{ad,CH_3-\text{func},TEA} - W_{ad,CH_3-\text{func},60\%MeOH}$$

$$= 2(\gamma_{TEA} - \gamma_{60\%MeOH}) - \left(W_{CH_3-TEA} - W_{CH_3-60\%MeOH}\right) - (W_{\text{func}-TEA} - W_{\text{func}-60\%MeOH})$$

$$\text{(S14)}$$

From equations (S2a) and (S2b), the second and the third parenthesis on the right-hand side of equation (S14) can be expressed as

$$W_{CH_3-TEA} - W_{CH_3-60\%MeOH} = (\gamma_{TEA} - \gamma_{60\%MeOH}) - \left(\gamma_{CH_3-TEA} - \gamma_{CH_3-60\%MeOH}\right) \quad \text{(S15a)}$$

$$W_{\text{func}-TEA} - W_{\text{func}-60\%MeOH} = (\gamma_{TEA} - \gamma_{60\%MeOH}) - (\gamma_{\text{func}-TEA} - \gamma_{\text{func}-60\%MeOH}) \quad \text{(S15b)}$$

Equations (S15a) and (S15b) can be combined with equation (S14) to give

$$\Delta G_{tr,total} = W_{ad,CH_3-\text{func},TEA} - W_{ad,CH_3-\text{func},60\%MeOH}$$

$$= \left(\gamma_{CH_3-TEA} - \gamma_{CH_3-60\%MeOH}\right) + \left(\gamma_{\text{func}-TEA} - \gamma_{func-60\%MeOH}\right) \quad \text{(S16)}$$

From equation (S7), the adhesive forces measured between pure methyl SAMs and functionalized SAMs in aqueous TEA ($F_{ad,CH_3-\text{func},TEA}$) or aqueous TEA containing 60 vol% MeOH ($F_{ad,CH_3-\text{func},60\%MeOH}$) can be converted to the work of adhesion ($W_{ad,CH_3-\text{func},TEA}$ or $W_{ad,CH_3-\text{func},60\%MeOH}$) as

$$\frac{F_{ad,CH_3-\text{func},TEA}}{R} = \frac{3}{2}\pi W_{ad,CH_3-\text{func},TEA} \quad \text{(S17a)}$$

$$\frac{F_{ad,CH_3-\text{func},60\%MeOH}}{R} = \frac{3}{2}\pi W_{ad,CH_3-\text{func},60\%MeOH} \quad \text{(S17b)}$$

Equation (S16) can be combined with equations (S9a), (S9b), (S17a), and (S17b) and rearranged to arrive at

$$\gamma_{\text{func}-TEA} - \gamma_{\text{func}-60\%MeOH}$$

$$= \frac{2}{3\pi R}\left(F_{ad,CH_3-\text{func},TEA} - F_{ad,CH_3-\text{func},60\%MeOH}\right) - \frac{1}{3\pi R}\left(F_{ad,CH_3-CH_3,TEA} - F_{ad,CH_3-CH_3,60\%MeOH}\right)$$

(S18)

The left-hand side of equation (S18) corresponds to the transfer free energy of the functionalized SAM ($\Delta G_{tr,\text{func}} = \gamma_{\text{func}-TEA} - \gamma_{\text{func}-60\%MeOH}$). Additionally, $\Delta G_{tr,\text{func}}$ can be expressed as the sum of enthalpic ($\Delta H_{tr,\text{func}}$) and entropic ($T\Delta S_{tr,\text{func}}$) contributions at temperature (T) as

$$\Delta G_{tr,\text{func}} = \Delta H_{tr,\text{func}} - T\Delta S_{tr,\text{func}} \quad \text{(S19)}$$

The transfer entropy of the functionalized SAM ($\Delta S_{tr,\text{func}}$) can be evaluated by taking the derivative of the transfer free energy with respect to temperature at constant pressure (p)

$$\Delta S_{tr,\text{func}} = -\left(\frac{\partial \Delta G_{tr,\text{func}}}{\partial T}\right)_p$$

$$= -\frac{1}{3\pi R}\frac{\partial}{\partial T}\left[2\left(F_{ad,CH_3-\mathrm{func},TEA} - F_{ad,CH_3-\mathrm{func},60\%MeOH}\right) - \left(F_{ad,CH_3-CH_3,TEA} - F_{ad,CH_3-CH_3,60\%MeOH}\right)\right]_p$$

(S20)

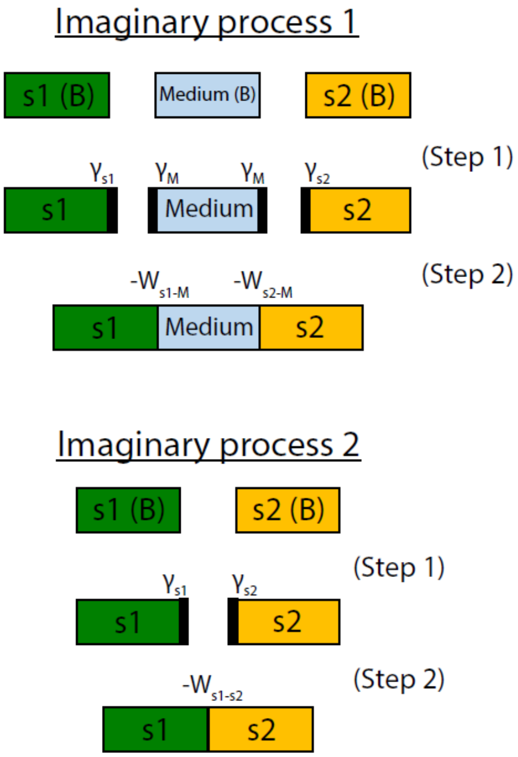


Figure S6. Imaginary processes used to evaluate the transfer free energy of a functionalized SAMs("s2").

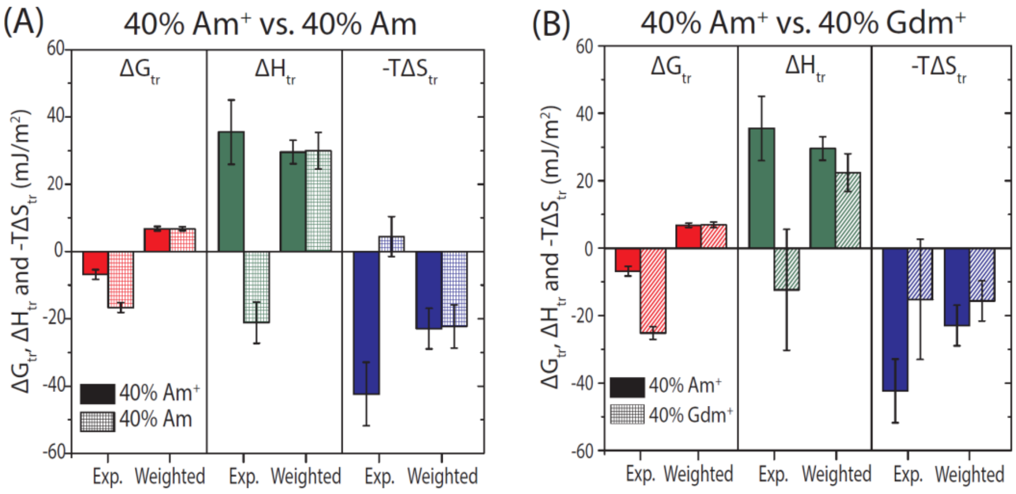


Figure S7. Transfer free energy (ΔG_{tr}, red), transfer enthalpy (ΔH_{tr}, green), and transfer entropy multiplied by temperature (T) ($-T\Delta S_{tr}$, blue) for (A) mixed ammonium/methyl surfaces ("40% Am$^+$", solid fill) versus mixed amine/methyl surfaces ("40% Am", grid lines fill) and (B) mixed ammonium/methyl surfaces ("40% Am$^+$", solid fill) versus mixed guanidinium/methyl surfaces ("40% Gdm$^+$", grid lines fill). Values obtained from experiments performed with mixed monolayers are labeled as "Exp.", and values calculated as averages of pure component monolayers (weighted by atomic composition) are labeled as "Weighted".

Section S2. Estimation of transfer free energies from solvation free energy of single ions

Inspection of Figure 4 reveals that the protonation of amine groups in mixed monolayers (achieved by lowering the pH from 10.5 to 3.5) causes an increase in the transfer free energy of the mixed ammonium/methyl surfaces, whereas the transfer free energies for the pure amine or ammonium surfaces are pH-independent. In an attempt to provide physical insight into these trends, we compared the transfer free energies to solvation free energies of single molecules (i.e., amines or ammonium salts).

We made two assumptions to enable the above-mentioned comparison. The first assumption was that the hydration behaviors of amine groups in pure- or mixed-component SAMs are similar to NH_3 (or NH_4^+) and CH_3NH_2 (or $CH_3NH_3^+$), respectively. The second assumption was that a counter ion (Cl^-) binds to the ammonium cation (NH_4^+ and $CH_3NH_3^+$ at low pH) but does not bind to the neutral amine group (NH_3 and CH_3NH_2 at high pH). To account for the association/dissociation of counter ions to the protonated amine groups, we considered four possible scenarios for the transfer process from aqueous TEA containing 60 vol% MeOH to aqueous TEA (Table S2). For instance, the third scenario assumes that the ammonium cations are initially associated with Cl^- ions in 60 vol% MeOH, that the salt is transferred from 60 vol% MeOH to aqueous TEA (associated state with Cl^- ions), and then the Cl^- ions dissociate from the ammonium cation in the aqueous TEA.

Guided by the above considerations, we estimated the free energy change upon transfer of NH_3/NH_4^+ (i.e., pure amine surfaces) or $CH_3NH_2/CH_3NH_3^+$ (i.e., mixed amine/methyl surfaces) from 60 vol% MeOH added to aqueous TEA into aqueous TEA using equations (S21) to (S24)). We used the solvation free energies reported in the literatures[4-7] to make the estimates. We note that solvation free energies measured in water-methanol mixtures are not reported for amine or ammonium species except NH_4^+. The addition of 60 vol% MeOH into water, however, does not significantly change in magnitude of the solvation free energy for NH_4^+.[8] Thus, we used the solvation free energies measured in pure MeOH in our calculation.

For the pure-component ammonium surfaces, the transfer free energies (ΔG_{tr}) for the four possible scenarios (S1-S4) are evaluated as

S1: $\Delta G_{tr} = G_{solv,TEA}\,(NH_4^+Cl^-) - G_{solv,60\%MeOH}\,(NH_4^+Cl^-)$ (S21a)

$= (-160.8) - (-159.7) = -1.1$ kcal / mol (= -1.8 kT)

S2: $\Delta G_{tr} = [G_{solv,TEA}\,(NH_4^+) + G_{solv,TEA}\,(Cl^-)] - [G_{solv,60\%MeOH}\,(NH_4^+) + G_{solv,60\%MeOH}\,(Cl^-)]$ (S21b)

$= [(-85.2) + (-74.5)] - [(-85.6) + (-71.5)] = -2.6$ kcal / mol (= 4.4 kT)

S3: $\Delta G_{tr} = [G_{solv,TEA}\,(NH_4^+Cl^-) - G_{solv,60\%MeOH}\,(NH_4^+Cl^-)] + \Delta G_{dissociation,TEA}\,(NH_4^+Cl^-)$ (S21c)

$= [(-160.8) - (-159.7)] + (1.1) = 0.0$ kcal / mol (= 0.0 kT)

S4: $\Delta G_{tr} = \{[G_{solv,TEA}\,(NH_4^+) + G_{solv,TEA}\,(Cl^-)] - [G_{solv,60\%MeOH}\,(NH_4^+) + G_{solv,60\%MeOH}\,(Cl^-)]\} +$
$\Delta G_{association,TEA}\,(NH_4^+Cl^-)$ (S21d)

$= [(-85.2) + (-74.5)] - [(-85.6) + (-71.5)] + (-1.1) = -3.7$ kcal / mol (= -6.2 kT)

where $G_{solv,TEA}\,(NH_4^+Cl^-)$ and $G_{solv,60\%MeOH}\,(NH_4^+Cl^-)$ are the solvation free energies of associated NH_4^+ and Cl^- ions in aqueous TEA or 60 vol% MeOH added to aqueous TEA, respectively. $G_{solv,TEA}\,(NH_4^+)$ and $G_{solv,TEA}\,(Cl^-)$ are the solvation free energies of single NH_4^+ and Cl^- ions in aqueous TEA, respectively. $G_{solv,60\%MeOH}\,(NH_4^+)$ and $G_{solv,60\%MeOH}\,(Cl^-)$ are the solvation free energies of single NH_4^+ and Cl^- ions in 60 vol% MeOH added to aqueous TEA, respectively. $\Delta G_{association,TEA}\,(NH_4^+Cl^-)$ and $\Delta G_{dissociation,TEA}\,(NH_4^+Cl^-)$ are the Coulomb free energy changes upon moving NH_4^+ and Cl^- ions from infinite separation to the separation found in a salt (i.e., for association). For the pure-component amine surfaces, the transfer free energy (ΔG_{tr}) was evaluated as

$$\Delta G_{tr} = G_{solv,TEA}\ (NH_3) - G_{solv,60\%MeOH}\ (NH_3) \quad (S22)$$

$$= (-4.3) – (-4.9) = 0.6\ kcal / mol\ (= 0.9\ kT)$$

where $G_{solv,TEA}$ (NH_3) and $G_{solv,60\%MeOH}$ (NH_3) are the solvation free energies of NH_3 in aqueous TEA or 60 vol% MeOH added to aqueous TEA, respectively.

Similarly, for the mixed-component ammonium surfaces, the transfer free energies (ΔG_{tr}) for four possible scenarios (S1-S4) are described as

S1: $\Delta G_{tr} = G_{solv,TEA}\ (CH_3NH_3^+Cl^-) - G_{solv,60\%MeOH}\ (CH_3NH_3^+Cl^-) \quad (S23a)$

$$= (-152.0) – (-148.7) = -3.3\ kcal / mol\ (= -5.5\ kT)$$

S2: $\Delta G_{tr} = [G_{solv,TEA}\ (CH_3NH_3^+) + G_{solv,TEA}\ (Cl^-)] – [G_{solv,60\%MeOH}\ (CH_3NH_3^+) + G_{solv,60\%MeOH}\ (Cl^-)] \quad (S23b)$

$$= [(-76.4) + (-74.5)] – [(-74.6) + (-71.5)] = -4.8\ kcal / mol\ (= -8.1\ kT)$$

S3: $\Delta G_{tr} = [G_{solv,TEA}\ (CH_3NH_3^+\ Cl^-) - G_{solv,60\%MeOH}\ (CH_3NH_3^+Cl^-)] + \Delta G_{dissociation,TEA}\ (CH_3NH_3^+Cl^-) \quad (S23c)$

$$= [(-152.0) – (-148.7)] + (1.1) = -2.2\ kcal / mol\ (= -3.7\ kT)$$

S4: $\Delta G_{tr} = \{[G_{solv,TEA}\ (CH_3NH_3^+) + G_{solv,TEA}\ (Cl^-)] – [G_{solv,60\%MeOH}\ (CH_3NH_3^+) + G_{solv,60\%MeOH}\ (Cl^-)]\} + \Delta G_{association,TEA}\ (CH_3NH_3^+Cl^-) \quad (S24d)$

$$= [(-76.4) + (-74.5)] – [(-74.6) + (-71.5)] + (-1.1) = -5.9\ kcal / mol\ (=10.0\ kT)$$

where $G_{solv,TEA}$ ($CH_3NH_3^+Cl^-$) and $G_{solv,60\%MeOH}$ ($CH_3NH_3^+Cl^-$) are the solvation free energies of associated $CH_3NH_3^+$ and Cl^- ions in aqueous TEA or 60 vol% MeOH added to aqueous TEA, respectively. $G_{solv,TEA}$ ($CH_3NH_3^+$) and $G_{solv,TEA}$ (Cl^-) are the solvation free energies of single $CH_3NH_3^+$ and Cl^- ions in aqueous TEA, respectively. $G_{solv,60\%MeOH}$ ($CH_3NH_3^+$) and $G_{solv,60\%MeOH}$

(Cl^-) are the solvation free energies of single $CH_3NH_3^+$ and Cl^- ions in 60 vol% MeOH added to aqueous TEA, respectively. $\Delta G_{association,TEA}$ ($NH_4^+Cl^-$) and $\Delta G_{dissociation,TEA}$ ($CH_3NH_3^+$ Cl^-) are the Coulomb free energy changes upon moving $CH_3NH_3^+$ and Cl^- ions from infinite separation to the separation found in a salt. For the mixed-component amine surfaces, the transfer free energy (ΔG_{tr}) was evaluated as

$$\Delta G_{tr} = G_{solv,TEA}\ (CH_3NH_2) - G_{solv,60\%MeOH}\ (CH_3NH_2) \quad \text{(S24)}$$

$$= (-4.6) – (-4.55) = -0.05\ (= -0.08\ kT)$$

where $G_{solv,TEA}$ (CH_3NH_2) and $G_{solv,60\%MeOH}$ (CH_3NH_2) are the solvation free energies of CH_3NH_2 in aqueous TEA or 60 vol% MeOH added to aqueous TEA, respectively.

To enable a comparison of the above-calculated transfer free energies to our experimental measurements with surfaces, we converted the transfer free energies of pure- and mixed-component amine SAMs obtained from our experiment (Figure 4) into transfer free energies per thiol for each surfaces (1 thiol / 0.214 nm^2 for pure amine surfaces and 1 thiol / 0.428 nm^2 for mixed amine/methyl surfaces)[9]. These values are shown in Figure S8. Inspection of Figure S8 reveals that the behaviors of the molecules in bulk solution do not capture how the charge status of amine groups in pure- and mixed-component surfaces changes transfer free energies.

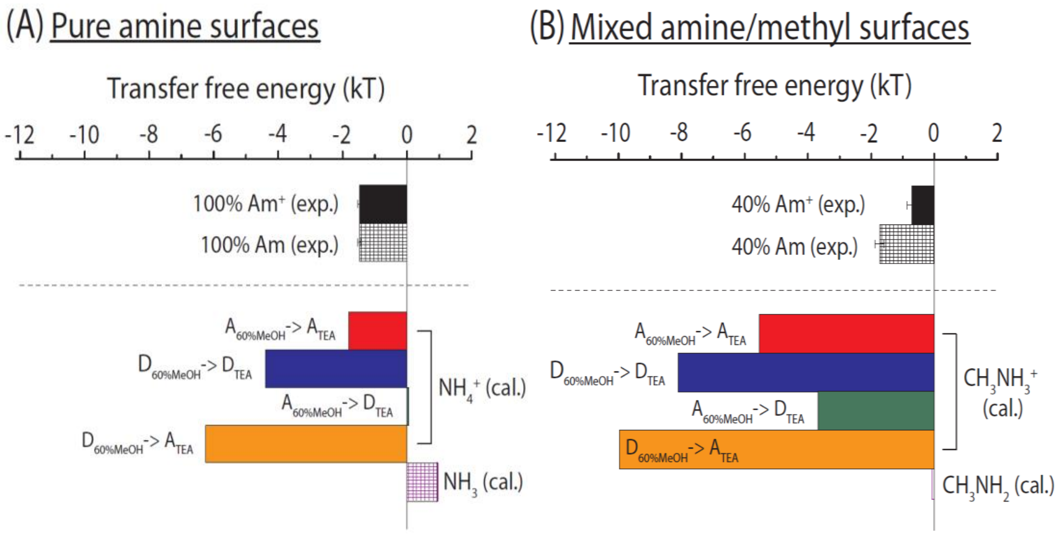


Figure S8. Experimentally-determined transfer free energies (per thiol) of (A) pure- and (B) mixed-component amine surfaces at pH 3.5 (solid black) and 10.5 (grid black), respectively. For comparison, the calculated transfer free energies of (A) NH_3/NH_4^+ and (B) $CH_3NH_2/CH_3NH_3^+$, are shown, respectively. Results corresponding to the four scenarios for association/dissociation of counter ions are shown in color: red (S1), blue (S2), green (S3), or yellow (S4), respectively. The calculated transfer free energies of amine species (NH_3 and CH_3NH_2) are colored in purple (grid).

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