SUPPORTING INFORMATION for

Nanoscale forces between basal mica surfaces in dicarboxylic acid solutions: implications for clay aggregation in the presence of soluble organic acids

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Supporting Information contains 17 pages, 1 figure and 8 tables.
**TABLE S1.** Chosen previous works studying adsorption of low molecular weight, soluble organic acids onto clay minerals and clay aggregation behavior in the presence of these organic acids.

| year | authors | title | mineral | organic molecules | methods | adsorption characteristics | face-specific information | reference |
|------|---------|-------|---------|-------------------|---------|--------------------------|--------------------------|-----------|
| 1972 | Rashid et al. | Interactions of a marine humic acid with clay minerals and a natural sediment. | chlorite, illite, kaolinite, natural sediments | humic acid | batch adsorption, XRD, thermogravimetric analysis, infrared spectroscopy, chemical modelling | Sorption of humic acid is higher in the presence of NaCl. Humic acid adsorption is reversible. Humic acid does not intercalate into interlayer spaces of clays. The work indicates that humic acid bonds via electrostatic and van der Waals forces, with a small proportion of humic acid chemically bonded with clays via -COOH groups. The authors suggest that the sorption is the highest in regions with highest proportion of broken bonds. | no | Geoderma 8 (1972) 11 - 27 |
| 1994 | Zhou et al. | The formation of humic coatings on mineral particles under simulated estuarine conditions—a mechanistic study | kaolinite, vermiculite | humic and fulvic acids | batch adsorption, specific surface area measurements | Humic acids are more likely to adsorb by chemisorption, whereas more hydrophilic organic molecules are physisorbed. There is no face specific information, although the authors suggest that sorption is larger for smaller clay particles due to higher amount of broken edges. | no | Water Research 28 (1994) 571-579 |
| Year | Authors | Title | Clay Type | Organic Acid | Methodology | Summary |
|------|---------|-------|-----------|--------------|-------------|---------|
| 1997 | Kubicki et al. | Bonding Mechanisms of Salicylic Acid Adsorbed onto Illite Clay: An ATR-FTIR and Molecular Orbital Study | illite | salicylic acid | batch adsorption, ATR-FTIR, molecular orbital calculations | The authors report strong inner-sphere sorption of salicylic acid onto illite. Although no face-specific experimental data has been presented, the authors suggest that salicylic acid bond to illite clay edges by forming covalent bonds (Al-O-C) between oxygen from the carboxylic group and Al from the edge Al³⁺ octahedral binding sites. |
| 1998 | Kretzschmar et al. | Influence of pH and Humic Acid on Coagulation Kinetics of Kaolinite: A Dynamic Light Scattering Study | kaolinite | humic acid | batch coagulation experiments, dynamic light scattering | Humic acid stabilizes colloidal suspensions of kaolinite. The authors suggest that this effect is related to humic acid binding onto amphoteric clay edges, and prevents electrostatic attraction between clay faces and edges. At high ionic strength steric repulsion is additionally considered as a possible mechanisms that enhances colloidal stability. |
| 1998 | Ward & Brady | Effect of Al and organic acids on the surface chemistry of kaolinite | kaolinite, quartz, corundum | formate, acetate, oxalate | batch adsorption, potentiometric titrations, liquid chromatography | The authors report pH dependent sorption of organic acids onto kaolinite and corundum. The sorption of oxalate onto kaolinite is stronger than of formate and acetate. The authors suggest that sorption onto kaolinite occurs at Al sites on kaolinite edges as negligible sorption occurs for silica but substantial for oxide - corundum. |
| Year | Authors | Study Title | Minerals/Compounds | Methods | Results/Findings | Journal/Reference |
|------|---------|-------------|--------------------|---------|-----------------|------------------|
| 1999 | Kubicki et al. | Attenuated total reflectance Fourier-transform infrared spectroscopy of carboxylic acids adsorbed onto mineral surfaces | Quartz, albite, illite, kaolinite and montmorillonite | Carboxylic acids: acetic, oxalic, citric, benzoic, salicylic and phthalic | Batch adsorption, ATR-FTIR, UV/visible spectroscopy, molecular orbital calculations | No chemisorption in aqueous phase. Chemisorption of carboxylic acids onto clays is facilitated by Fe-hydroxides present within the clay matrix. Although the experimental adsorption data is not face-specific, the authors discuss possible bonding sites on mineral surfaces. | Geochimica et Cosmochimica Acta 63 (1999) 2709-2725 |
| 1999 | Tombacz et al. | Particle aggregation in complex aquatic systems | Montmorillonite, kaolinite, aluminium oxide | Humate, gallate, salicylate | Batch aggregation, dynamic light scattering, acid-base titration | Organic anions increase colloidal stability of clay suspensions. The authors suggest that the increased colloidal stability is due to preferential binding of organic anions at Al-OH sites at broken clay edges. | Colloids and Surfaces A 151 (1999) 233-244 |
| 1999 | Liu & Gonzalez | Adsorption/Desorption in a System Consisting of Humic Acid, Heavy Metals, and Clay Minerals | Montmorillonite | Humic acid | Batch adsorption, UV-Vis, AAS | In the absence of metal ions, the sorption of humic acid decreases with the increasing pH. Divalent ions promote humic acid sorption. Cationic bridging is proposed as the dominant adsorption mechanisms in the presence of metal ions. | Journal of Colloid and Interface Science 218 (1999) 225-232 |
| 2000 | Namjesnik-Dejanovic & Maurice | Conformations and aggregate structures of sorbed natural organic matter on muscovite and hematite | Muscovite, hematite | Natural organic matter (NOM) | AFM topography | NOM adsorbs better on mica in the presence of Ca$^{2+}$ than Na$^+$. NOM sorbs in complex structures and aggregates on mica basal plane depending on pH and ionic composition. | Geochimica et Cosmochimica Acta 65; 7 (2000) 1047-1057 |
| Year | Authors | Title | Clay Type | Metal(s) | Method | Surface Specificity | Results | Journal |
|------|---------|-------|-----------|----------|--------|---------------------|---------|---------|
| 2001 | Specht & Frimmel | An in situ ATR-FTIR study on the adsorption of dicarboxylic acids onto kaolinite in aqueous suspensions | kaolinite | dicarboxylic acids, hydroxybenzoic acids and resorcinol | in situ ATR-FTIR | no | Inner-sphere complexation of dicarboxylic acids with kaolinite with one or two O atoms of -COOH groups bound to kaolinite surface at low pH values, below 6. At higher pH values, the authors suggest outer-sphere complexation via water molecules. No face-specific results and no discussion on the role of edges or basal surfaces on dicarboxylic acids adsorption is provided. | Phys. Chem. Chem. Phys. (2001) 3, 544 |
| 2002 | Tunega et al. | Theoretical Study of Adsorption Sites on the (001) Surfaces of 1:1 Clay Minerals | kaolinite | acetic acid | Quantum chemical calculations | yes: basal faces (001) | Acetate anion binds to kaolinite surface via hydrogen bonds. Adsorption is much stronger on octahedral kaolinite surface (hydrogen bonds between carboxylic groups and kaolinite surface hydroxyl groups). Adsorption via hydrogen bond is much weaker on tetrahedral surface (hydrogen bonds between -COOH and basal oxygen atoms). | Langmuir 18 (2002) 139-147 |
| 2002 | Tunega et al. | Ab Initio Molecular Dynamics Study of Adsorption Sites on the (001) Surfaces of 1:1 Dioctahedral Clay Minerals | kaolinite | acetic acid | Molecular dynamics | yes: basal faces (001) | Acetate binding to kaolinite occurs via multiple hydrogen bonding and it is much stronger on octahedral surfaces than on tetrahedral surfaces of kaolinite. | J. Phys. Chem. B 106 (2002) 11515-11525 |
| 2003 | Aquino et al. | Adsorption of Organic Substances on Broken Clay Surfaces: A Quantum Chemical Study | kaolinite | acetic acid, acetate, and N-methylacetamid | DFT modelling | yes: basal faces (001) | Broken, defect sites on basal clay surfaces can enhance bonding of organic molecules via hydrogen bonds with -OH groups | Comput Chem 24 (2003) 1853–1863 |
| Year | Authors          | Title                                                                 | Clay Minerals/Clay Min. | Techniques/Models/Methods | Summary                                                                                                                                                                                                 | Journal/Reference |
|------|------------------|----------------------------------------------------------------------|-------------------------|---------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------|
| 2003 | Lackovic et al.  | Modeling the adsorption of citric acid onto Muloorina illite and related clay minerals | illite, goethite, kaolinite | citric acid | batch adsorption, potentiometric titrations, ATR-FTIR, surface complexation models | The authors report pH-dependent sorption of citric acid onto clays. Kaolinite adsorbs the highest amount of citric acid between pH 4.5 and 7, while illite between pH 5 and 7. Sorption is smaller both at lower and higher pHs. Authors suggest only outer-sphere adsorption of citrate on illite and kaolinite edges and no evidence of adsorption on negatively charged silica faces of both kaolinite and illite. | Journal of Colloid and Interface Science 267 (2003) 49–59 |
| 2004 | Labille et al.   | Flocculation of colloidal clay by bacterial polysaccharides: effect of macromolecule charge and structure | montmorillonite | polysaccharides: dextran, succinoglycan, soligel, xanthan, MWAP71 | batch aggregation, rheology | Neutral polysaccharides adsorb by Ca$^{2+}$ bridging. The authors suggest that negatively charged polysaccharides can strongly adsorb only onto pH-dependent clay edges at low pH. | Journal of Colloid and Interface Science 284 (2005) 149-156 |
| 2007 | Kang & Xing      | Adsorption of Dicarboxylic Acids by Clay Minerals as Examined by in Situ ATR-FTIR and ex Situ DRIFT | kaolinite, montmorillonite | dicarboxylic acids: succinic acid, glutaric acid, adipic acid, and azelaic acid | experiments: ATR-FTIR, DRIFT spectroscopies | Outer-sphere complexation in aqueous media dominates at all pHs. Inner-sphere complexation is additionally significant at pH 4 and major under dry conditions. Adsorption is higher for more hydrophobic molecules. No face-specific information about the adsorption, however, it is suggested that sorption is higher at low pH due to abundance of positive charges at clay edges. | Langmuir 23 (2007) 7024-7031 |
| Year | Authors | Title  | Methods | Results |
|------|---------|--------|---------|---------|
| 2007 | Majzik & Tombacz | Interaction between humic acid and montmorillonite in the presence of calcium ions I. Interfacial and aqueous phase equilibria: Adsorption and complexation | montmorillonite, humic acid | Humic acid adsorbs through Ca²⁺ bridges on basal montmorillonite surfaces and directly on clay edges by inner-sphere complexation to Al-OH groups. Although the presented batch adsorption experiments are not face-specific, the authors discuss in detail different nature of binding on edges and basal planes, and support their findings by acid-base titration. |
| 2008 | Liu et al. | Surface complexes of acetate on edge surfaces of 2:1 type phyllosilicate: Insights from density functional theory calculation | 2:1 type clay, acetate | Both inner and outer-sphere complexation is possible at clay edges. Formation of covalent bonds and H-bonds is predicted. |
| 2009 | Furukawa et al. | Aggregation of montmorillonite and organic matter in aqueous media containing artificial seawater | montmorillonite, humic acid, chitin | Organic molecules adsorb onto montmorillonite and stabilize colloidal suspensions. The authors suggest that colloidal stability is increased in the presence of organic molecules, which adsorb onto clay edges and introduce steric repulsion. |
| 2009 | Kitadai et al. | In situ ATR-IR investigation of L-lysine adsorption on montmorillonite | montmorillonite, L-lysine | Cationic lysine adsorbs onto the negatively charged montmorillonite surface mainly via electrostatic interactions. The authors discuss possible sorption both on clay edges and on basal planes depending on pH conditions; however, no face-specific data is obtained. |
| Year | Authors | Title | Clay | Humic Acid | Methods | Comments |
|------|---------|-------|------|------------|---------|----------|
| 2010 | Martinez et al. | Surface binding site analysis of Ca²⁺-homoionized clay-humic acid complexes | kaolinite, illite | humic acids | Dissolved organic carbon (DOC), Acid-base titration, Zeta potential, FTIR | Ca²⁺ affects conformation of humic acid and promotes its adsorption onto clays by cation bridging. Face-specific adsorption is not discussed in detail; however, the role of edge reactive surface groups is mentioned. |
| 2012 | Zhang et al. | Integrated investigations on the adsorption mechanisms of fulvic and humic acids on three clay minerals | kaolinite, smectite, vermiculite | fulvic and humic acids | NMR, liquid chromatography, UV-Vis spectroscopy, FTIR, XPS | Hydrophobic interactions are involved in sorption of humic and fulvic acids onto clays. The acids can bind via ligand exchange mechanism (inner-sphere complexation), particularly for smectite and vermiculite. Fe-bearing vermiculate promotes ligand exchange to larger extent. Fe facilitates sorption via cation bridging. Authors do not explicitly point to sorption on clay edges or basal surfaces, but suggest that intercalation of acids in the interlayer space of 2:1 type clays was negligible. |
| 2012 | Jiang et al. | Effects of inorganic and organic anions on the stability of illite and quartz soil colloids in Na-, Ca-and mixed Na–Ca systems | quartz, illite | oxalate, formate | batch aggregation | Higher colloidal stability of illite suspensions in the presence of oxalate anions is attributed to the inner-sphere oxalate complexation at illite edges. |
| Year | Authors       | Title                                                                 | Clay Type   | Acid       | Method                          | Findings                                                                                                                                                                                                 | Journal                                    |
|------|---------------|----------------------------------------------------------------------|-------------|------------|---------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------|
| 2014 | Ramos et al.  | Kinetics of montmorillonite dissolution: An experimental study of the effect of oxalate | montmorillonite | oxalic acid | batch adsorption, batch dissolution study, DR-FTIR | Authors suggest that oxalate adsorbs mainly on montmorillonite edges by forming complexes with amphoteric aluminol sites. The authors point to electrostatic repulsion between negatively charged montmorillonite basal surface and oxalate, which limits or even prevent oxalate adsorption at the basal surface. As such, they only expect oxalate adsorption at crystal edges. | Chemical Geology 363 (2014) 283-292         |
| 2014 | Yeasmin et al. | Influence of mineral characteristics on the retention of low molecular weight organic compounds: A batch sorption–desorption and ATR-FTIR study | kaolinite, illite, montmorillonite, ferrihydrite, goethite | citric acid, oxalic acid, glutamic acid, alanine, phenylalanine, lysine | batch adsorption, ATR-FTIR spectroscopy | The authors report higher sorption of anionic carboxylic and glutamic compared to the other compounds. Cationic lysine displayed a high affinity for clays with permanent negative charge. Inner- and outer-sphere complexes has been suggested for sorption of oxalate and citrate on kaolinite and goethite. Sorption of negatively charged carboxylic acids onto phyllosilicate is generally suggested to occur on clay edges. | Journal of Colloid and Interface Science 432 (2014) 246–257 |
| 2017 | Liu et al.    | Complexation of carboxylate on smectite surfaces                       | smectite     | acetate    | first principles molecular dynamics (FPMD) | The authors model that acetate forms inner-sphere complexes on (110) smectite edges in a very limited mildly acidic pH range and on (010) edges in the whole pH range. Ca\(^{2+}\) promotes binding of acetate in the interlayer space. | Phys. Chem. Chem. Phys. (2017) 19, 18400 |
| Year | Authors | Title | Soil Organic Matter – Mineral Interactions | Minerals | Functional Groups | Methodology | Results | Notes |
|------|---------|-------|-------------------------------------------|----------|-------------------|-------------|---------|-------|
| 2017 | Newcomb et al. | Developing a molecular picture of soil organic matter – mineral interactions by quantifying organo–mineral binding | muscovite, goethite | various functional groups (e.g. -COOH modified AFM tip) | AFM force spectroscopy | -COOH functionality binds to mica most strongly. The -COOH binding strength decreases both with the increasing pH and ionic strength. Ca\(^{2+}\) enhances -COOH binding to mica. | yes: basal faces (001) | Nature Communications 8: 396 |
| 2018 | Xue et al. | Interaction between low molecular weight carboxylic acids and muscovite: Molecular dynamic simulation and experiment study | muscovite | carboxylic acids: formic, acetic, propionic, butyric acids | modelling: MD; experiments: ATR-FTIR, AFM mapping, contact angle | Outer sphere adsorption on basal (001) muscovite faces is studied: the authors point to hydrogen bonds between H atom of -COOH functional group of carboxylic acid and O atom of muscovite. | yes: basal faces (001) | Colloids and Surfaces A 559 (2018) 8-17 |
TABLE S2. Parameters of low pH and high pH dicarboxylic acid and inorganic control solutions used in the experiments shown in Figures 2, 3 and 4 (pH was only adjusted with NaOH or HCl).

| mica surfaces | solution | mica-mica (MM) experiments (Figures 2, 3, 4) |
|---------------|----------|------------------------------------------|
|               |          | low pH (measured) | low pH (PhreeqC) | high pH (pH adjusted) | added NaOH (mM) |
| set | mica | average adhesion in H₂O (mN/m) | dicarboxylic acid (DA) | concentration (mM) | Figures 2, 3 | Figures 2, 4 | measured | measured | 50 |
| 1 | 1 | 47.31 | C2 oxalic | 1,40 | 1,47 | 8,40 | 99,8 |
| 2 | 2 | 59.16 | C2 oxalic | 1,33 | - | 8,27 | 100,7 |
| 1 | 3 | 62.03 | C3 malonic | 1,95 | 2,02 | 8,35 | 99,4 |
| 2 | 4 | - | C3 malonic | 1,89 | - | 8,33 | 100,8 |
| 1 | 5 | 61.50 | C4 succinic | 2,60 | 2,66 | 8,42 | 100,3 |
| 2 | 6 | 49.61 | C4 succinic | 2,49 | - | 8,33 | 101,0 |
| 1 | 7 | 48.32 | C5 glutaric | 2,65 | 2,72 | 8,48 | 100,8 |
| 2 | 8 | 49.06 | C5 glutaric | 2,61 | - | 8,33 | 101,1 |
| 1 | 9 | 21.08 | C6 adipic | 2,68 | 2,79 | 8,32 | 101,1 |
| 2 | 10 | 41.32 | C6 adipic | 2,67 | - | 8,41 | 101,1 |
| 1 | 11 | 45.15 | C7 pimelic | 2,70 | 2,81 | 8,36 | 100,9 |
| 2 | 12 | 54.08 | C7 pimelic | 2,67 | - | 8,36 | 100,6 |

pH control experiments

| - | 13 | 14 | 15 | 16 |
| - | 66.17 | 56.34 | 107.19 | 118.05 |
| HCl | 2 | 10 | 34 | NaCl |
| 2,70 | 2,00 | 1,47 | - | 150 |
| - | - | - | 1,40 | - |
| - | - | - | - | 8.30 |
| - | - | - | - | ~0.01 |
**TABLE S3.** Parameters of high pH adipic acid (C6) and CaCl₂:NaCl inorganic control solutions used in the experiments shown in Figure 5, with pH partially adjusted with varying concentrations of Ca(OH)₂.

| mica surfaces pair | average adhesion in H₂O (mN/m) | solution | C6 concentration (mM) | Ca²⁺ (mM) | pH | Ca(OH)₂ (mM) | NaOH (mM) |
|-------------------|-------------------------------|----------|-----------------------|-----------|----|--------------|-----------|
| 17 18             | 56.16 61.36                  | C6 adipic acid | 50            | 1         | 8.3-8.4 | 1            | 99        |
|                   |                               |           |                       | 5         |      |              | 5         |
|                   |                               |           |                       | 20        |      |              | 20        |

| mica surfaces pair | average adhesion in H₂O (mN/m) | solution | C6 concentration (mM) | Ca²⁺ (mM) | pH | Ca(OH)₂ (mM) | NaOH (mM) |
|-------------------|-------------------------------|----------|-----------------------|-----------|----|--------------|-----------|
| 19 20             | 113.50 44.51                  | CaCl₂ + NaCl | 0              | 1         | 8.3-8.4 | 1            | 99        |
|                   |                               |           |                       | 5         |      |              | 5         |
|                   |                               |           |                       | 20        |      |              | 20        |

**TABLE S4: Parameters of high pH dicarboxylic acid solutions with 5 mM of Ca²⁺ used in the experiments shown in Figure 6.**

| mica surfaces pair | average adhesion in H₂O (mN/m) | dicarboxylic acid (DA) | DA concentration (mM) | Ca²⁺ (mM) | pH | Ca(OH)₂ (mM) | NaOH (mM) |
|-------------------|-------------------------------|----------------------|-----------------------|-----------|----|--------------|-----------|
| 21                | 103.20                        | C3 malonic start     | 50            | 5         | 8.3-8.4 | 5            | 90        |
|                   |                               | C4 succinic          |                       |           |      |              |           |
|                   |                               | C5 glutaric          |                       |           |      |              |           |
|                   |                               | C6 adipic            |                       |           |      |              |           |
|                   |                               | C7 pimelic           |                       |           |      |              |           |
|                   |                               | C8 malonic end       |                       |           |      |              |           |
**TABLE S5**: Dissociation constants of diprotic dicarboxylic acids. The dissociation constants were adapted from: **a)** Bhattacharyya, L., & Rohrer, J. S. (Eds.). (2012). Applications of ion chromatography for pharmaceutical and biological products. John Wiley & Sons; **b)** Daniele, P. G., *et al*. (1985). Journal of the Chemical Society, Dalton Transactions, (11), 2353-2361; **c)** Nakajima, D., *et al*. (2014). Applied surface science, 321, 364-370.

| Dicarboxylic Acid | Dissociation Constants |
|------------------|------------------------|
|                  | $pK_{a1}$ | $pK_{a2}$ |
| Oxalic $H_2C_2O_4$ | 1.04$^a$ | 3.82$^a$ |
| $HC_2O_4^- + H^+ = H_2C_2O_4$ | $C_2O_4^{2-} + H^+ = HCO_2O_4^-$ |
| Malonic $H_4C_3O_4$ | 2.70$^b$ | 5.36$^b$ |
| $H_3C_3O_4^- + H^+ = H_4C_3O_4$ | $H_2C_3O_4^{2-} + H^+ = H_3C_3O_4^-$ |
| Succinic $H_6C_4O_4$ | 4.05$^b$ | 5.26$^b$ |
| $H_5C_4O_4^- + H^+ = H_6C_4O_4$ | $H_4C_4O_4^{2-} + H^+ = H_5C_4O_4^-$ |
| Glutaric $H_6C_5O_4$ | 4.13$^c$ | 5.03$^c$ |
| $H_7C_5O_4^- + H^+ = H_6C_5O_4$ | $H_6C_5O_4^{2-} + H^+ = H_7C_5O_4^-$ |
| Adipic $H_{10}C_6O_4$ | 4.26$^a$ | 5.03$^a$ |
| $H_9C_6O_4^- + H^+ = H_{10}C_6O_4$ | $H_8C_6O_4^{2-} + H^+ = H_9C_6O_4^-$ |
| Pimelic $H_{12}C_7O_4$ | 4.31$^a$ | 5.08$^a$ |
| $H_{11}C_7O_4^- + H^+ = H_{12}C_7O_4$ | $H_{10}C_7O_4^{2-} + H^+ = H_{11}C_7O_4^-$ |
**TABLE S6.** Association constants for formation of Na\(^+\) and Ca\(^{2+}\) complexes with dicarboxylic acids. The association constants were adapted from: **a)** Daniele, P. G., *et al.* (2008). Coordination chemistry reviews, 252(10-11), 1093-1107; **b)** Daniele, P. G., *et al.* (1985). Journal of the Chemical Society, Dalton Transactions, (11), 2353-2361; **c)** Peacock, J. M., & James, J. C. (1951). Journal of the Chemical Society (Resumed), 2233-2239; **d)** Topp, N. E., & Davies, C. W. (1940). Journal of the Chemical Society (Resumed), 87-93. Some association constants for glutaric, adipic and pimelic acid were not accessible in the literature.

| Dicarboxylic Acid | Association Constants |
|-------------------|-----------------------|
|                   | **Na\(^+\)** | **Ca\(^{2+}\)** |
| **C2 Oxalic**     | \(0.71^a\)  | \(3.27^a\)  |
| \(\text{C2O}_4^{2-} + \text{Na}^+ = \text{NaC}_2\text{O}_4^-\) | \(\text{C2O}_4^{2-} + \text{Ca}^{2+} = \text{CaC}_2\text{O}_4\) |
| **C3 Malonic**    | \(0.91^a\)  | \(2.39^a\)  |
| \(\text{H}_2\text{C}_3\text{O}_4^{2-} + \text{Na}^+ = \text{NaH}_2\text{C}_3\text{O}_4^-\) | \(\text{H}_2\text{C}_3\text{O}_4^{2-} + \text{Ca}^{2+} = \text{CaH}_2\text{C}_3\text{O}_4\) |
| \(-0.04^a\) | \(0.39^a\)  |
| \(\text{H}_3\text{C}_3\text{O}_4^- + \text{Na}^+ = \text{NaH}_3\text{C}_3\text{O}_4\) | \(\text{H}_3\text{C}_3\text{O}_4^- + \text{Ca}^{2+} = \text{CaH}_3\text{C}_3\text{O}_4^+\) |
| **C4 Succinic**   | \(0.85^a\)  | \(2.24^a\)  |
| \(\text{H}_4\text{C}_4\text{O}_4^{2-} + \text{Na}^+ = \text{NaH}_4\text{C}_4\text{O}_4^-\) | \(\text{H}_4\text{C}_4\text{O}_4^{2-} + \text{Ca}^{2+} = \text{CaH}_4\text{C}_4\text{O}_4\) |
| \(-\) | \(0.70^b\)  |
| \(\text{H}_5\text{C}_4\text{O}_4^- + \text{Ca}^{2+} = \text{CaH}_5\text{C}_4\text{O}_4^+\) |
| **C5 Glutaric**   | -  | \(1.76^c\)  |
| \(\text{H}_6\text{C}_5\text{O}_4^{2-} + \text{Ca}^{2+} = \text{CaH}_6\text{C}_5\text{O}_4\) |
| **C6 Adipic**     | -  | \(2.19^d\)  |
| \(\text{H}_8\text{C}_6\text{O}_4^{2-} + \text{Ca}^{2+} = \text{CaH}_8\text{C}_6\text{O}_4\) |
| **C7 Pimelic**    | -  | -  |

\(\text{log}_{10} K\)
**TABLE S7:** DLVO fitting and theoretical parameters for forces measured in low pH dicarboxylic acids and HCl inorganic controls shown in Figure 3C. $\psi_0$ is surface potential; $\lambda_{EXP}$ is fitted Debye length; $\lambda_D$ is theoretical Debye length calculated based on solutions ionic strength (IS).

| pH | Solution       | $\psi_0$ (mV) | $\lambda_{EXP}$ (nm) | $\lambda_D$ (nm) | IS  (mM) |
|----|----------------|---------------|----------------------|-----------------|--------|
| 1.4| HCl            | 72.9 ± 10.9   | 1.3 ± 0.1            | 1.54            | 39.8   |
| 1.4| C2 oxalic acid | 87.9 ± 9.7    | 1.6 ± 0.1            | 1.54            | 39.0   |
| 2.0| HCl            | 36.5 ± 2.2    | 3.0 ± 0.1            | 3.05            | 10.0   |
| 2.0| C3 malonic acid| 55.5 ± 3.1    | 3.3 ± 0.1            | 2.99            | 9.9    |
| 2.7| HCl            | 26.0 ± 1.4    | 6.8 ± 0.1            | 6.81            | 2.0    |
| 2.6| C4 succinic acid| 36.9 ± 1.2   | 6.5 ± 0.3            | 6.35            | 2.2    |
| 2.7| C5 glutaric acid| 25.5 ± 2.5   | 6.7 ± 0.1            | 6.81            | 2.0    |
| 2.7| C6 adipic acid | 33.3 ± 1.9    | 7.4 ± 0.1            | 7.39            | 1.7    |
| 2.7| C7 pimelic acid| 32.5 ± 1.1    | 7.4 ± 0.3            | 7.62            | 1.6    |

Electrical double layer forces and surface potentials $\psi_0$ were estimated using the linear superposition approximation (LSA) method at constant potential (CP-LSA), adapted from Israelachvili (Intermolecular and surface forces. 3rd ed.; Academic Press: 2011; see Figure 14.10, Chapter 14, page 317 therein):

\[
EDL_{CP-LSA} = \kappa \sqrt{R^2 Z e^{-\kappa D}}, \quad \text{where} \quad \kappa = \frac{\sqrt{\sum_i C_i e^2 z_i^2 \varepsilon_0 \varepsilon \kappa T}}{Z}
\]

\[
Z = 64 \pi \varepsilon_0 \varepsilon (kT/e)^2 \tan \left(\frac{z e \psi_0}{4kT}\right)
\]

$\kappa^{-1}$ is Debye length (m$^{-1}$), $C_i$ is bulk concentration of each ion species $i$ in the solution (M), $z$ is ion valency, $\varepsilon_0$ is electrical permittivity of vacuum (F/m), $\varepsilon$ is the water dielectric constant, $k$ is the Boltzmann constant, $T$ is temperature (K), $R$ is the radius of the SFA cylindrical samples (m), and $D$ is the distance between the surfaces (m). As the amount of divalent species in dicarboxylic acid solutions is negligible at low pH, we assumed monovalent electrolytes composed of $HX^-$ and $H^+$ species, where $X^{2-}$ is a fully dissociated dicarboxylic anion. Neutral $H_2X$ species do not contribute to EDL repulsion.
TABLE S8: Theoretical and fitted Debye lengths for high pH dicarboxylic acid solutions and NaCl inorganic control for forces shown in Figure 4A. Theoretical Debye lengths were calculated based on the solution ionic strength (IS), including Na complexation if the association constants were available. Na complexation has been modelled in PhreeqC software using association constants summarized in Table S5. \(X^2^-\) is a fully dissociated dicarboxylic anion.

| pH | Solution | DA concentration (mM) | \(\lambda_{\text{EXP}}\) (nm) | \(\lambda_D\) (with NaX\(^-\)) (nm) | IS (with NaX\(^-\)) (mM) | \(\lambda_D\) (no NaX\(^-\)) (nm) | IS (no NaX\(^-\)) (mM) |
|----|----------|------------------------|----------------|----------------|-----------------------------|----------------|-----------------------------|
| 8.3 | NaCl | - | 0.9 ± 0.1 | - | - | 150 | |
| | C2 oxalic | 50 | 1.4 ± 0.1 | 0.83 | 136.1 | | |
| | C3 malonic | | 1.2 ± 0.1 | 0.85 | 129.9 | | |
| | C4 succinic | | 1.0 ± 0.1 | 0.84 | 132.0 | | |
| | C5 glutaric | | 0.8 ± 0.1 | | | 0.79 | |
| | C6 adipic | | 0.9 ± 0.1 | | | | |
| | C7 pimelic | | 0.9 ± 0.1 | | | | |
FIGURE S1: Representative forces (F) normalized with the radius of contact curvature (R) measured as a function of surface separation (D) in high pH (8.3) NaCl control experiment, with ionic strength (IS) of 150 mM. The measured experimental Debye length was $\lambda_{\text{EXP}} = 0.9 \pm 0.1$ nm. The inset plot shows variation of adhesion measured in a representative experiment.