Supporting information for: A Means to an Interface: Investigating Monoethanolamine Behavior at an Aqueous Surface

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DFT method evaluation

VSF spectra for aqueous 10 M MEA solutions were calculated with six combinations of xc–functionals (B3LYP, B2PLYP and MP2) and basis sets (6–311++G(2d,2p) or aug–cc–pVTZ). The calculated spectra were compared to experimental spectra in both ssp– and sps–polarization, with deviation in peak position and relative intensity of spectral peaks used to determine the best match between calculated and experimental spectra. Supporting Figure 1 shows the six calculated ssp spectra offset from the 10 M MEA ssp experimental spectra, with the main contributing experimental peaks highlighted with vertical guides. For both the bending and stretching ssp spectra, the 6–311++G(2d,2p) basis set performs better than the aug–cc–pVTZ. Additionally, the B2PLYP and MP2 functionals better predict experimental peak positions.

Supporting Figure 2 shows calculated and experimental sps spectra in the CH stretching region of the vibrational spectra. Only sps spectra of the (a) B2PLYP and (b) MP2 xc–functionals are shown, as they were the closest matches to the experimental ssp spectra. However, in sps
Figure 1: Experimental (dashed black) and calculated (colored) VSF spectra for 10 M MEA solution in ssp in the bending region (top) and the stretching region (bottom). Calculations for B3LYP—6311G+(2d,2p) (red solid); B3LYP—aug-ccpVTZ (red dashed); B2PLYP—6311G+(2d,2p) (blue solid); B2PLYP—aug-ccpVTZ (blue dashed); MP2—6311++G(2d,2p) (green solid); and MP2—aug-ccpVTZ (green dashed) are shown. Spectra offset for clarity with guide lines for experimental peaks.
the MP2 functional no longer accurately predicts experimental spectra; rather the B2PLYP is fa-
vored. As demonstrated in Supporting Figure 2(a) (along with Figure 4 in the manuscript), the
B2PLYP–6311G++(2d,2p) is the preferred functional–basis set combination for calculating the
MEA spectra.

Figure 2: Experimental (dashed black) and calculated (colored) VSF spectra for 10 M MEA so-
lution in sps in the CH stretching region. Calculations for (a) B2PLYP—6311G++(2d,2p) (blue
solid) and (b) MP2–6311++G(2d,2p) (green solid) shown.

DFT structures

Nine unique MEA gas–phase DFT structures were matched (via dihedral angle binning) with MEA
conformers extracted from the MD simulations. The DFT and MD conformers were defined based
on 4 unique dihedral angles (D1–D4), as shown in Figure 3, where D1=N–C–C–O; D2=C–C–
O–H; D3=C–C–N–H\textsuperscript{a}; and D4=C–C–N–H\textsuperscript{b}. The optimized DFT structures’ dihedral angles are
listed in Table 1 along with the range of dihedrals used to define the MD structures. For the MD
structural assignments, the range of angles applies to rotation in both directions.

The MD conformers’ dihedral distributions were extracted from the simulations and matched
to representative DFT structures. The optimized DFT structures correspond to peaks in the MD
dihedral distributions, as shown in Figure 4, with the exception of the MEA1 conformer whose anti configuration does not correspond to a maximum in the dihedral distribution but was included to fully represent the conformational space. Unsurprisingly, the MD conformer matching showed most MEA molecules adopt gauche conformations (> 90%) while few MEA molecules adopt anti conformations. The largest abundance of MD conformers were assigned to DFT structure MEA14 (~20%).

Table 1: DFT structures and energies calculated at B3LYP/6-311++G(2d,2p) level of theory. Conformer ranges for MD simulations that matched the DFT structures.

<table>
<thead>
<tr>
<th>MD Conformer</th>
<th>DFT energy (Hartree)</th>
<th>DFT Dihedral Angle (°)</th>
<th>Dihedral Range (°) for MD Assignments</th>
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<tr>
<td></td>
<td>D1</td>
<td>D2</td>
<td>D3</td>
</tr>
<tr>
<td>MEA1</td>
<td>-209.094229</td>
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<td>-68.7</td>
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<td>MEA10</td>
<td>-209.099279</td>
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<td>-43.8</td>
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<td>MEA11</td>
<td>-209.090517</td>
<td>70.5</td>
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<tr>
<td>MEA13</td>
<td>-209.093947</td>
<td>60.3</td>
<td>-76.4</td>
</tr>
<tr>
<td>MEA14</td>
<td>-209.096063</td>
<td>60.0</td>
<td>-177.6</td>
</tr>
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<td>MEA15</td>
<td>-209.095663</td>
<td>58.2</td>
<td>71.1</td>
</tr>
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<td>MEA16</td>
<td>-209.095583</td>
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<td>MEA17</td>
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<td>54.2</td>
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<td>MEA18</td>
<td>-209.096517</td>
<td>64.8</td>
<td>-169.9</td>
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</table>
Figure 4: MEA correlated MD dihedral distributions. Maxima are highlighted with representative structural cartoons and labeled with the corresponding DFT structures. Color scheme for z–axis follows that outlined in the manuscript, where cooler colors represent less population and warmer colors represent greater population.
Deuterated ssp spectra of 10 M MEA

Spectra in the bending region of the vibrational spectrum were acquired in both H₂O and D₂O to assist in mode assignments. In Supporting Figure 4(a), spectra of the neat H₂O and D₂O interfaces are shown, with the free OH (1625 cm⁻¹) and free OD (∼1210 cm⁻¹) strongly contributing to observed signal. Supporting Figure 4(b) shows 10 M MEA solutions in different aqueous solvents: H₂O for the blue trace and D₂O for the purple trace. Exchange of the amine hydrogens with the solvent results in a loss of the peak at ∼1595 cm⁻¹ in the D₂O sample; however, retention of the peaks at 1448 cm⁻¹ and 1360 cm⁻¹ is observed.

![Figure 5](image)

Figure 5: Spectra acquired in bending region of vibrational spectrum in ssp–polarization. (a) H₂O (grey dashed) and D₂O (black solid) and (b) 10 M MEA in H₂O (blue) and 10 M MEA in D₂O (purple)

Gibbs adsorption calculations

Surface pressure, $\pi$, is plotted as a function of bulk MEA concentration in Supporting Figure 5(a). The Gibbs adsorption equations may be used to relate surface tension (or surface pressure) of a solute with surface excess concentrations, average area per molecule, the relative adsorption or the surface mole fraction of the solute.¹⁻⁴ In Equation 1, the maximum surface excess ($\Gamma_i$) can be
extracted from the surface pressure by performing a linear fit of the surface pressure values versus the natural log of the bulk activities, as shown in Supporting Figure 5(b).

\[
\Gamma_{MEA} = \frac{1}{RT} \left( \frac{\partial \pi}{\partial \ln a_{MEA}} \right)_{T,P} \tag{1}
\]

Figure 6: (a) MEA surface pressure (\(\pi\), mN/m) plotted as a function of bulk MEA concentration. Error bars are one standard deviation from the average of 3–10 data points. (b) MEA surface pressure plotted as a function of natural log of the MEA activities. The dashed line is a fit to the data.

Bulk concentrations of MEA were corrected to activities (\(\alpha_i\)) using the activity coefficients (\(\gamma_i\)) derived by Hilliard.\(^5\) The slope of the fit line in Figure 5 (b) was inverted to give the average area per molecule. For MEA, the average area per molecule was found to be \(\sim 126 \text{ Å}^2/\text{molecule}\).

Additionally, the surface mole fraction may be calculated from the Gibbs equation of relative adsorption (\(\Gamma_{2,1}\)) as outlined by Tyrode, et al.,\(^3\) via Equation 2.

\[
\Gamma_{MEA,H_2O} = -\frac{x \left( \frac{\partial \eta}{\partial x} \right)_{T,P}}{RT \left( 1 + x \frac{\partial \ln \gamma}{\partial x} \right)} = \Gamma_{MEA} - \Gamma_{H_2O} \cdot \frac{x}{1 - x} \tag{2}
\]

where \(x\) is the bulk mole fraction of MEA, \(\gamma\) is the activity coefficient from Hilliard, \(\eta\) is the surface tension of MEA, and \(\Gamma_{H_2O}\) and \(\Gamma_{MEA}\) are the surface excess concentrations of water and
MEA in $\mu$mol/m$^2$. Linearly fitting $\left( \frac{\partial \eta}{\partial x} \right)_{T,P}$ and $\left( \frac{\partial \ln \gamma}{\partial x} \right)$, as shown in Supporting Figure 6 (a) and (b), enables solving of $\Gamma_{MEA,H_2O}$ for each bulk mole fraction of MEA. Using the area per molecule

$$N_{Av}(\Gamma_{H_2O} a_{H_2O} + \Gamma_{MEA} a_{MEA}) = 10^{26}$$

$$m.f.s = \frac{\Gamma_{MEA}}{\Gamma_{MEA} + \Gamma_{H_2O}}$$

**Average molecular tilt**

Analysis of methylene group average molecular tilt has been extensively studied,\textsuperscript{4,6–8} and thus only a brief description of the analysis pertinent to the MEA system is included here.

$$\chi_{ssp,SS}(\theta) = 2 \cos(\theta)$$
\[ \chi_{ssp}, AS(\theta) = | -2.106 [\cos(\theta) - \cos^3(\theta)] | \] (6)

The results of this analysis for the 10 M MEA spectra are included in Supporting Table 1, where “A” refers to the fitted amplitudes of the peaks. Following the outline of methylene selection rules by Lu, et al., a relationship between the components of \( \chi^{(2)} \) and the vibrationally active components of \( \beta^{(2)} \) may be made via the orientation of the methylene group. For \( ssp \)-polarization these relations simplify to Equations 5 and 6, assuming standard methylene bond angles of 109.5° and \( C_{2v} \) symmetry.

Table 2: Parameters used for calculating the average molecular tilt for the methylene groups of MEA. Errors calculated from standard deviation of the fitted amplitudes.

<table>
<thead>
<tr>
<th></th>
<th>peak 1</th>
<th>peak 2</th>
<th>peak 3</th>
<th>peak 4</th>
<th>A(SS)</th>
<th>A(AS)</th>
<th>A(SS)/A(AS)</th>
<th>( \theta^\circ )</th>
</tr>
</thead>
<tbody>
<tr>
<td>\textit{ssp} 10M bulk MEA</td>
<td>2845</td>
<td>2873</td>
<td>2920</td>
<td>2936</td>
<td>3.21</td>
<td>1.76</td>
<td>1.82</td>
<td>46±6</td>
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<tr>
<td>\textit{ssp} 5M bulk MEA</td>
<td>2845</td>
<td>2873</td>
<td>2920</td>
<td>2936</td>
<td>2.17</td>
<td>0.95</td>
<td>2.27</td>
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<tr>
<td>\textit{ssp} 1M bulk MEA</td>
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<td>2873</td>
<td>2920</td>
<td>2936</td>
<td>0.80</td>
<td>0.40</td>
<td>1.97</td>
<td>45±10</td>
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</tbody>
</table>

References

(1) Rosen, M. J. Surfactants and interfacial phenomena; Wiley Online Library, 2004; Vol. 3.


