

Supplementary Information

The Effect of CO₂ Loading on Alkanolamine Absorbents in Aqueous Solutions

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Table S1. System specification of mixed MEA/W/CO₂ systems at various CO₂ loadings. Number of molecules of each constituent and box dimensions (nm).

| Cpd | CO ₂ - Loading | | | |
|-----------------------------------|---------------------------|--------|--------|--------|
| | 0.0 | 0.1 | 0.3 | 0.5 |
| MEA | 1600 | 1280 | 640 | - |
| MEACOO ⁻ | - | 160 | 480 | 800 |
| MEA H ⁺ | - | 160 | 480 | 800 |
| H ₂ O | 12640 | 12640 | 12640 | 12640 |
| CO ₂ | 64 | 64 | 64 | 64 |
| Simulation box dimensions | | | | |
| without unreacted CO ₂ | 8.1212 | 8.1213 | 8.1295 | 8.1431 |
| with unreacted CO ₂ | 8.1400 | 8.1403 | 8.1487 | 8.1632 |

Table S2. System specification of mixed DEAB/W/CO₂ systems at various CO₂ loadings. Number of molecules of each constituent and box dimensions (nm).

| Cpd | CO ₂ -Loading | | | | |
|-----------------------------------|--------------------------|---------|---------|---------|---------|
| | 0.0 | 0.169 | 0.364 | 0.578 | 0.815 |
| DEAB | 1020 | 740 | 492 | 295 | 164 |
| DEABH ⁺ | - | 280 | 528 | 725 | 856 |
| HCO ₃ ⁻ | - | 64 | 214 | 455 | 806 |
| CO ₃ ²⁻ | - | 108 | 157 | 135 | 25 |
| H ₂ O | 28980 | 28808 | 28609 | 28390 | 28149 |
| CO ₂ | 64 | 64 | 64 | 64 | 64 |
| Simulation box dimensions | | | | | |
| without unreacted CO ₂ | 10.4490 | 10.4066 | 10.3819 | 10.3864 | 10.4146 |
| with unreacted CO ₂ | 10.4662 | 10.4215 | 10.3954 | 10.3974 | 10.4264 |

Table S3. Diffusion coefficients (x10⁻⁵ cm² s⁻¹) of pure and aqueous MEA at T=298K: experiment versus simulations.

| Mixture compositions | Our results | Experiments | AUA4(+SPCE water) | AUA4 (+TIP4P2005 water) |
|----------------------|-------------|--|-------------------|-------------------------|
| Pure MEA | 0.094±0.001 | 0.055^a | 0.113 ± 0.006 | 0.113 ± 0.006 |
| 30/70 wt/wt | 0.663±0.028 | 0.69^b and 0.58^c | 0.548 ± 0.001 | 0.422 ± 0.002 |

| | | | | |
|--------------------------|-------------|---|---------------|---------------|
| MEA/water | | | | |
| 06/94 wt/wt MEA/water | 1.078±0.011 | 0.984^b and 1.00^d | 1.030 ± 0.040 | 0.835 ± 0.004 |

[^a] M. N. Rodnikova, F. M. Samigullin, I. A. Solonina, and D. A. Sirotkin. Molecule mobility and structure of polar liquids. *J. Struct. Chem.* **2014**, *55*, 256-262.

[^b] Hikita, H.; Ishikawa, H.; Uku, K.; Murakami, T. Diffusivities of Mono-, Di-, and Triethanolamines in Aqueous Solutions. *J. Chem. Eng. Data* **1980**, *25*, 324-325.

[^c] Thomas, W.J.; McK. Nicholl, E. Diffusion measurements for ethanolamine water systems with a wavefront-shearing interferometer. *J. appl. Chem.* **1967**, *17*, 251-255.

[^d] Snijder, E.D.; te Riele, M.J.M.; Versteeg, G.F.; van Swaaij, W.P.M. Diffusion Coefficients of Several Aqueous Alkanolamine Solutions. *J. Chem. Eng. Data* **1993**, *38*, 475-480.

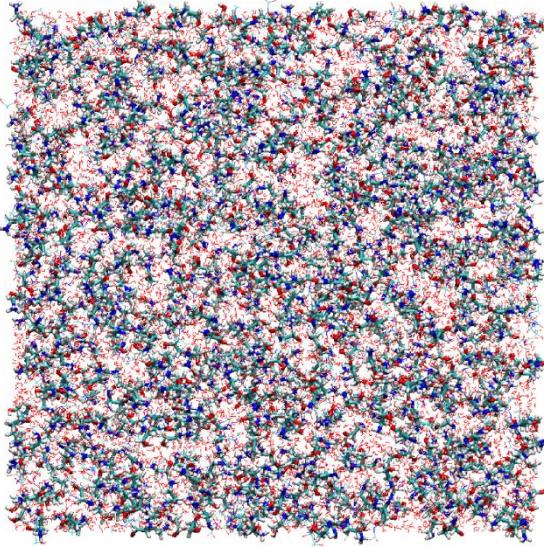


Figure S1. Snapshots of MD simulation (box length 8.1295 nm) for the case of CO₂-loaded aqueous MEA solution at 0.3 CO₂ loading. Unreacted MEA molecules are displayed as sticks, other molecules (water, CO₂, MEACOO⁻ and protonated MEAH⁺) are shown as wireframes.

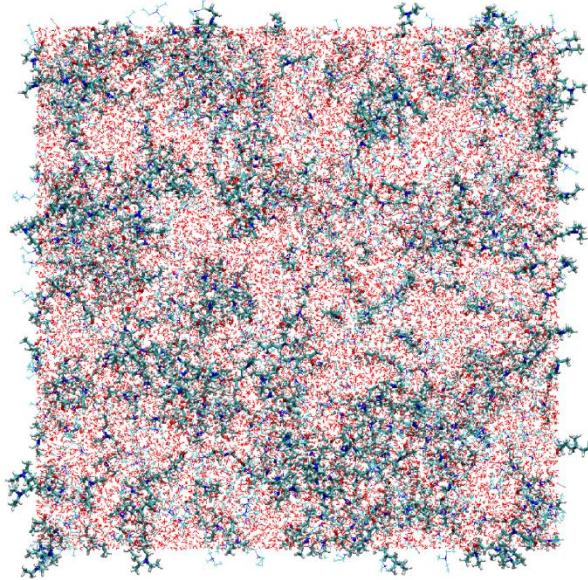


Figure S2. Snapshot of MD simulation (box length of 10.3954 nm) for the case of CO₂-loaded aqueous DEAB at 0.364 CO₂ loading. Unreacted DEAB molecules are displayed as sticks, other molecules (water, CO₂, carbonate, bicarbonate, and protonated DEABH⁺) are shown as wireframes.

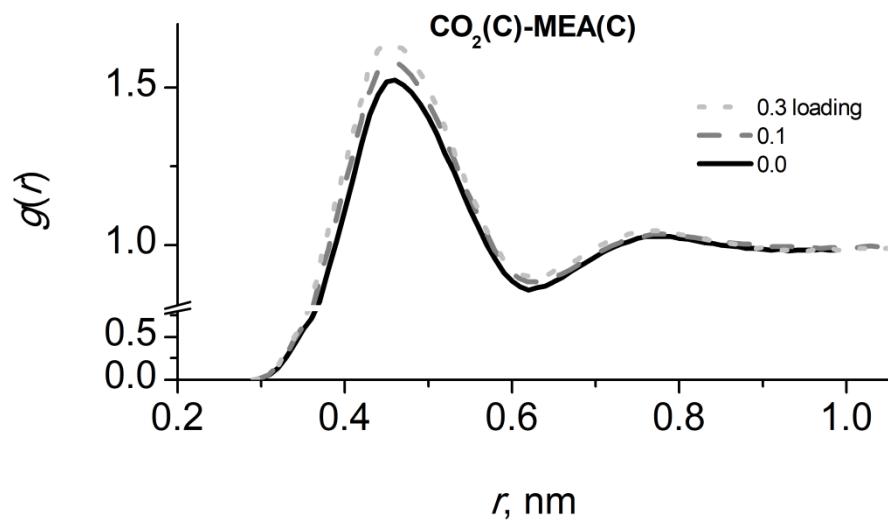


Figure S3. RDFs of CO₂(C)-MEA(C) interactions in the MEA/W/CO₂ mixture at various loadings.

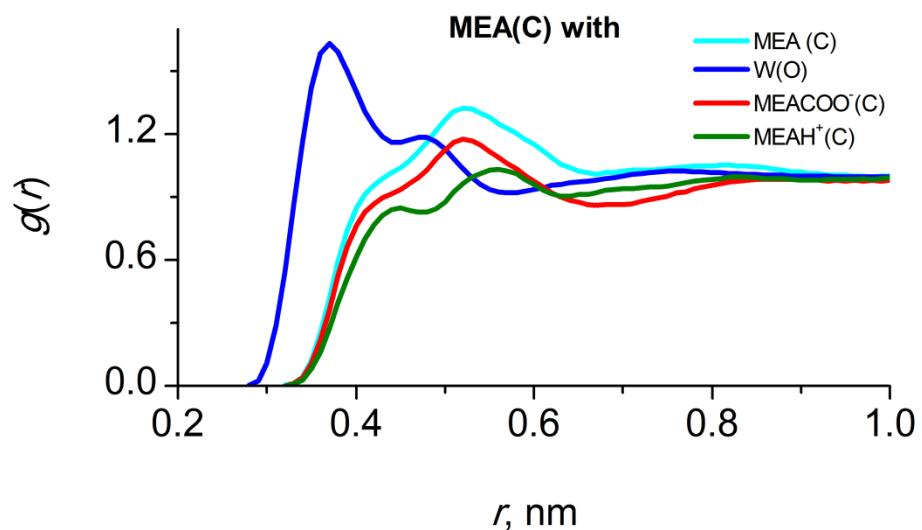


Figure S4. RDFs of MEA(C) interactions in the MEA/W/CO₂ mixture with other mixture species at CO₂-loading of 0.3.

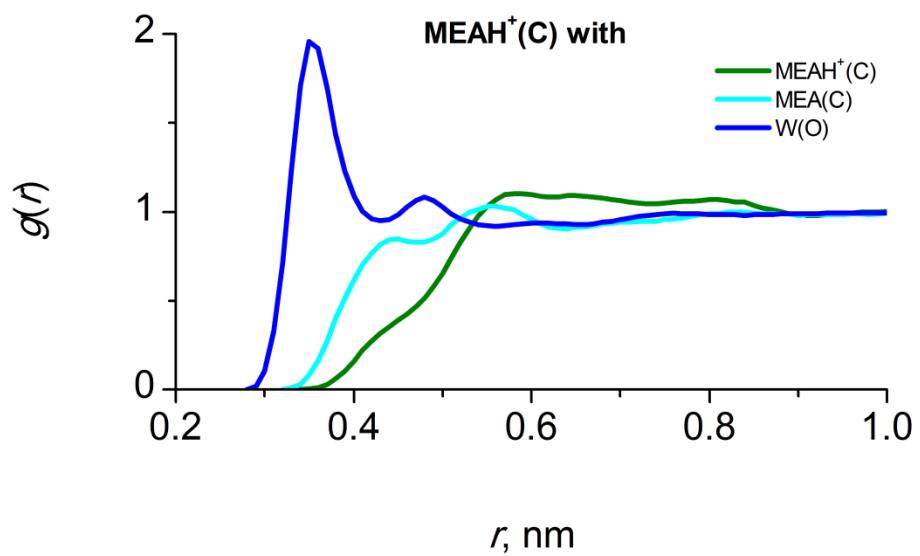


Figure S5. RDFs of $MEA^{+}(C)$ interactions in the MEA/W/ CO_2 mixture with other mixture species at CO_2 -loading of 0.3.

Table S4. Diffusion coefficients for the MEA/W/CO₂ mixture at 313 K.

| Loading | MEA | MEACOO ⁻ | MEA H ⁺ | CO ₂ | Water |
|---------|--------------------|---------------------|--------------------|--------------------|--------------------|
| 0.0 | 0.9795 ± 0.0091 | - | - | 2.0109 ± 0.0266 | 1.9811 ± 0.0006 |
| 0.1 | 0.8584 ± 0.0029 | 0.4749 ± 0.0010 | 0.5469 ± 0.011 | 1.7531 ± 0.0049 | 1.7844 ± 0.0039 |
| 0.3 | 0.6379 ± 0.0047 | 0.3142 ± 0.0069 | 0.3677 ± 0.0018 | 1.3406 ± 0.0050 | 1.4370 ± 0.0010 |
| 0.5 | - | 0.2233 ± 0.0086 | 0.2551 ± 0.0062 | 1.0088 ± 0.0075 | 1.1403 ± 0.0015 |

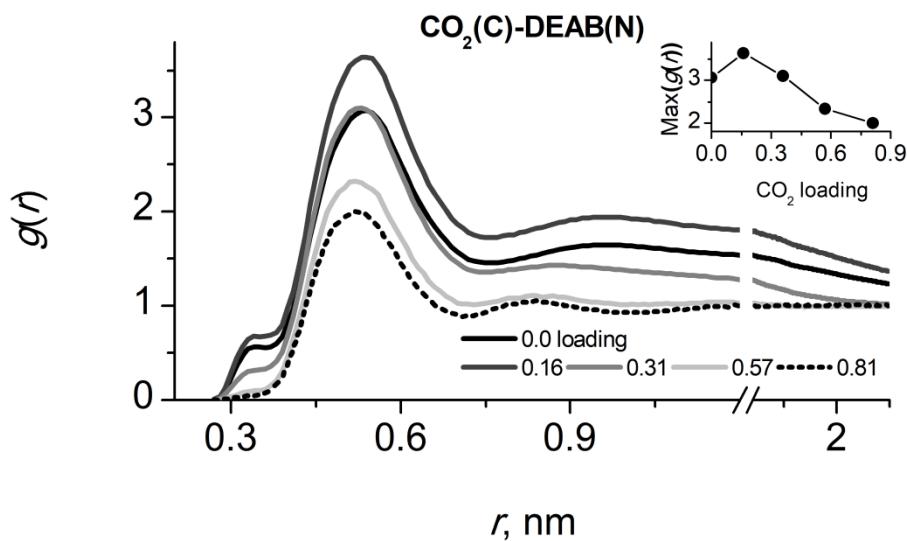


Figure S6. RDFs of CO₂(C) – DEAB(N) interactions in the DEAB/W/CO₂ mixture at various loadings.

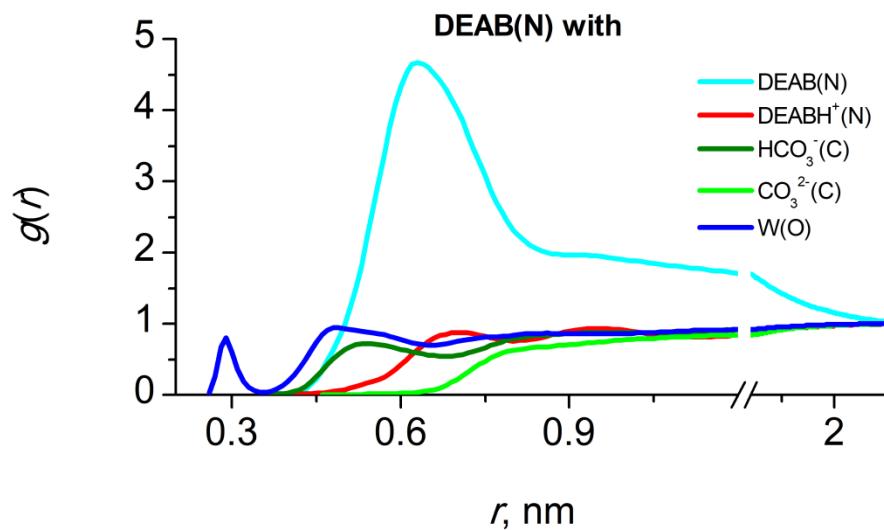


Figure S7. RDFs of DEAB(N) interactions in the DEAB/W/CO₂ mixture with other mixture species at CO₂-loading of 0.364.

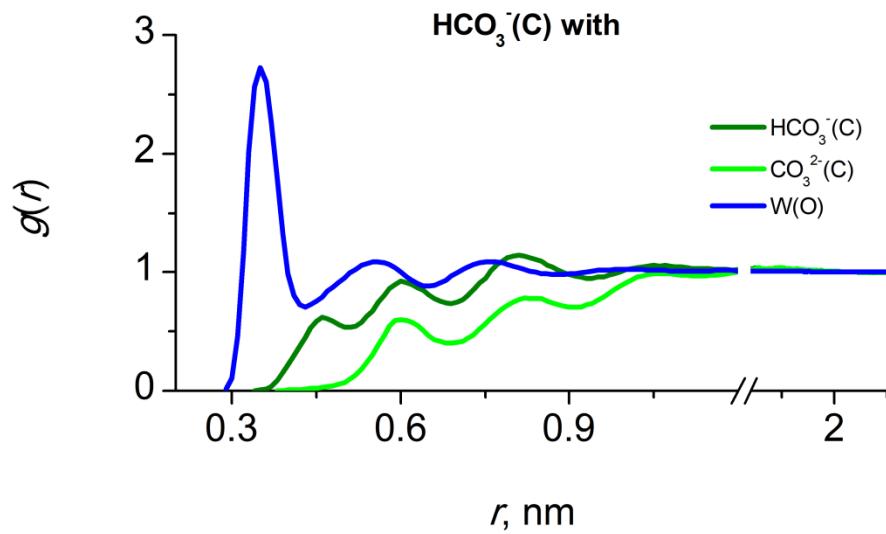


Figure S8. RDFs of HCO₃⁻(C) interactions in the DEAB/W/CO₂ mixture with other mixture species at CO₂-loading of 0.364.

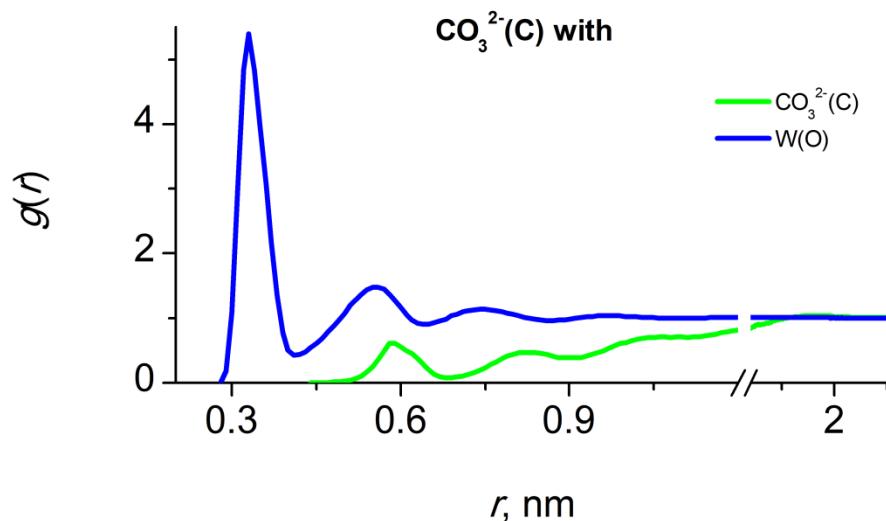


Figure S9. RDFs of CO₃²⁻(C) interactions in the DEAB/W/CO₂ mixture with other mixture species at CO₂-loading of 0.364.

Table S5. Simulation diffusion coefficients for various DEAB/W/CO₂ mixtures at 313 K.

| Cpd CO ₂ - Loading | DEAB | DEABH ⁺ | HCO ₃ ⁻ | CO ₃ ²⁻ | CO ₂ | Water |
|-------------------------------------|--------------------|--------------------|-------------------------------|-------------------------------|--------------------|--------------------|
| 0.0 | 0.3060 ± 0.0169 | - | - | - | 1.8371 ± 0.0224 | 2.5551 ± 0.0421 |
| 0.169 | 0.2871 ± 0.0157 | 0.5161 ± 0.0116 | 0.8757 ± 0.0026 | 0.5334 ± 0.0176 | 1.6701 ± 0.0101 | 2.0751 ± 0.0199 |
| 0.364 | 0.3224 ± 0.0164 | 0.4039 ± 0.0158 | 0.6678 ± 0.0042 | 0.4098 ± 0.0041 | 1.5216 ± 0.0055 | 1.6518 ± 0.0099 |
| 0.578 | 0.3341 ± 0.0170 | 0.3645 ± 0.0175 | 0.5952 ± 0.0080 | 0.3660 ± 0.0089 | 1.4626 ± 0.0127 | 1.5259 ± 0.0038 |
| 0.815 | 0.3740 ± 0.0155 | 0.3642 ± 0.0162 | 0.5783 ± 0.0067 | 0.3221 ± 0.0141 | 1.4491 ± 0.0171 | 1.5469 ± 0.0029 |

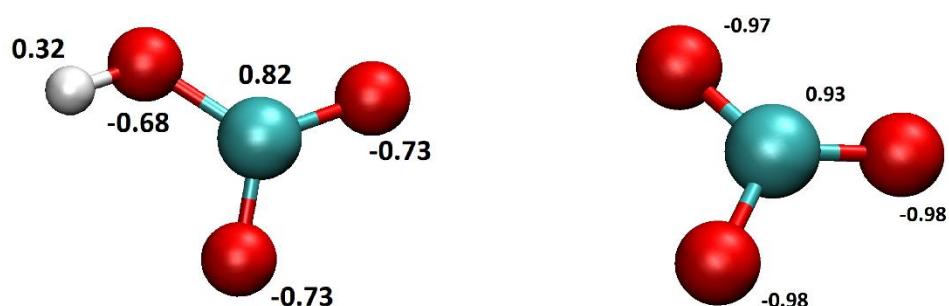


Figure S10. Calculated partial charges for bicarbonate and carbonate ions.