Supporting Information

# Interactions of CO<sub>2</sub> Anion Radical with Electrolyte Environments from First-Principles Simulations

Morgan M. Cencer,<sup>†§</sup> Chenyang Li,<sup>†§</sup> Garvit Agarwal,<sup>†1</sup> Reginaldo Jose Gomes Neto,<sup>‡</sup> Chibueze V. Amanchukwu,<sup>‡</sup> and Rajeev S. Assary<sup>†\*</sup>

<sup>†</sup>Materials Science Division, Argonne National Laboratory, Lemont, IL, 60439 <sup>‡</sup>Pritzker School of Molecular Engineering, The University of Chicago, Chicago, IL, 60637

Chemical Sciences and Engineering Division, Argonne National Laboratory, Lemont, IL, 60439

<sup>§</sup>These authors contributed equally to this work.

\*Email: assary@anl.gov

<sup>&</sup>lt;sup>1</sup> Present address: Schrödinger, Inc., New York, NY, 10036

### A. Quantum chemical calculations: Gaussian input details

a. All ADMP runs were started from checkpoint geometry from a static geometry optimization at 0 K. The Nuclear Kinetic Energy (NKE) values (in microHartrees) were calculated for each system at a temperature of 298.15 K using

$$NKE = \frac{3}{2}(N-1)k_BT,$$

where *N* is the total number of atoms,  $k_B$  is the Boltzmann constant (3.16681225 microHartree/K), and *T* is the temperature in Kelvin.

b. Gaussian input detail: Geometry optimization

#p opt(MaxCycles=200) SCF(XQC,MaxConventional=200) freq wb97xd/6-31+g(d,p)

c. ADMP simulations: Input line

#p ADMP(Maxpoints=5000,NKE=CalcFroSystem,StepSize=1000) wb97xd/jun-ccpVDZ scf(XQC,MaxConventional=200) geom=(crowd,Checkpoint) Guess=Read

d. Input line for ADMP simulations with implicit solvent:

#p ADMP(Maxpoints=5000,NKE= CalcFroSystem,StepSize=1000) wb97xd/jun-ccpVDZ scf(XQC,MaxConventional=200) geom=(crowd,Checkpoint) Guess=Read scrf(cpcm,solvent=SolventName)

Solvent name = (water, Tetrahydrofuran. Note that the tetrahydrofuran is used to model the implicit solvent interaction of DME solvent due to similarity in their dielectric constant.

e. All post simulation analysis of DFT calculations (i.e., measuring distances and angles) were completed using python (ASE, Numpy, and Pandas packages).

#### **B.** Calculation of complexation enthalpy $(\Delta H)$

e.g., for Li<sup>+</sup>–DME systems:

$$\Delta H_{complex}(Li^{+}, 3DME) = H(Li^{+}, 3DME) - H(Li^{+}) - 3H(DME),$$
  
$$\Delta H_{complex}(Li^{+}, CO_{2}^{-}, 3DME) = H(Li^{+}, CO_{2}^{-}, 3DME) - H(Li^{+}) - H(CO_{2}^{-}) - 3H(DME).$$

The binding enthalpy of a  $CO_2^-$  (*BE*<sub>CO2</sub>-) is calculated by:

$$\begin{split} BE_{CO_{2}^{-}} &= H(Li^{+}, CO_{2}^{-}, 3DME) - H(Li^{+}, 3DME) - H(CO_{2}^{-}) \\ &= \Delta H_{complex}(Li^{+}, CO_{2}^{-}, 3DME) - \Delta H_{complex}(Li^{+}, 3DME). \end{split}$$

NoneYesNone0NoneYesH2O1NoneYesH2O2NoneYesH2O3NoneYesDME1NoneYesDME2NoneYesDME3Li*YesH2O1Li*YesH2O2Li*YesH2O1Li*YesH2O3Li*YesDME1Li*YesDME1Li*YesDME1Li*YesDME3Li*YesDME3Li*YesDME3Li*YesNone0Na*YesH2O2Li*YesNone0Na*YesH2O3Na*YesH2O3Na*YesDME3Na*YesDME3K*YesDME3K*YesDME3K*YesH2O2K*YesDME3K*YesDME3K*YesDME3K*YesDME3K*YesDME3K*YesDME3Ma*YesDME3Ma*YesDME3Me4*YesDME3NMe4*YesDME3 <th>Cation</th> <th>CO<sub>2</sub>-</th> <th>Solvent Identity</th> <th>Number of Solvent</th>	Cation	CO <sub>2</sub> -	Solvent Identity	Number of Solvent
None         Yes         None         0           None         Yes         H2O         1           None         Yes         H2O         2           None         Yes         H2O         3           None         Yes         DME         1           None         Yes         DME         2           None         Yes         DME         3           Li*         Yes         DME         3           Li*         Yes         H2O         1           Li*         Yes         H2O         2           Li*         Yes         DME         2           Li*         Yes         DME         3           Li*         Yes         DME         2           Li*         Yes         DME         3           Na'         Yes         DME         3           Na'         Yes         DME         3           Na'         Yes         DME         1           Na'         Yes         DME         1           Na'         Yes         DME         2           Na'         Yes         DME         1			2	Molecules
None         Yes $H_2O$ 1           None         Yes $H_2O$ 3           None         Yes         DME         1           None         Yes         DME         1           None         Yes         DME         2           None         Yes         DME         3           Li*         Yes         None         0           Li*         Yes         H2O         1           Li*         Yes         H2O         3           Li*         Yes         DME         3           Li*         Yes         DME         1           Li*         Yes         DME         3           Li*         Yes         DME         3           Na*         Yes         None         0           Na*         Yes         DME         3           Na*         Yes         H2O         1           Na*         Yes         DME         1           Na*         Yes         DME         3           Na*         Yes         DME         3           K*         Yes         DME         3	None	Yes	None	0
NoneYes $H_2O$ 2NoneYesDME1NoneYesDME2NoneYesDME2NoneYesDME3Li <sup>+</sup> YesH_2O1Li <sup>+</sup> YesH_2O2Li <sup>+</sup> YesH_2O3Li <sup>+</sup> YesDME1Li <sup>+</sup> YesDME2Li <sup>+</sup> YesDME2Li <sup>+</sup> YesDME3Na <sup>+</sup> YesDME3Na <sup>+</sup> YesH_2O1Na <sup>+</sup> YesH_2O1Na <sup>+</sup> YesH_2O2Na <sup>+</sup> YesH_2O3Na <sup>+</sup> YesDME1Na <sup>+</sup> YesDME2Na <sup>+</sup> YesDME3K <sup>+</sup> YesDME3K <sup>+</sup> YesDME3K <sup>+</sup> YesH_2O1K <sup>+</sup> YesDME3K <sup>+</sup> YesDME3NMe4 <sup>+</sup> YesDME3NMe4 <sup>+</sup> YesDME3NMe4 <sup>+</sup> YesH_2O3NMe4 <sup>+</sup> YesDME1NMe4 <sup>+</sup> YesDME3NMe4 <sup>+</sup> YesDME3NMe4 <sup>+</sup> YesDME3NMe4 <sup>+</sup> YesDME3NMe4 <sup>+</sup> YesDME1NMe4 <sup>+</sup> YesDME1NMe4 <sup>+</sup>	None	Yes	H <sub>2</sub> O	1
NoneYesH2O3NoneYesDME1NoneYesDME2NoneYesDME3Li'YesH2O1Li'YesH2O2Li'YesH2O3Li'YesDME1Li'YesDME1Li'YesDME3Li'YesDME3Li'YesDME3Na'YesDME3Na'YesH2O1Na'YesH2O2Na'YesH2O3Na'YesH2O3Na'YesH2O3Na'YesDME1Na'YesDME3K'YesDME3K'YesDME3K'YesDME3K'YesH2O2K'YesH2O2K'YesDME1K'YesDME1K'YesDME3K'YesDME3K'YesDME3K'YesDME1Me4'YesDME1NMe4'YesDME3NMe4'YesDME3NMe4'YesDME3NMe4'YesDME3NMe4'YesDME1 <td>None</td> <td>Yes</td> <td>H<sub>2</sub>O</td> <td>2</td>	None	Yes	H <sub>2</sub> O	2
NoneYesDME1NoneYesDME2NoneYesDME3Li*YesNone0Li*YesH2O1Li*YesH2O3Li*YesDME1Li*YesDME1Li*YesDME1Li*YesDME2Li*YesDME3Na*YesNone0Na*YesH2O1Na*YesH2O1Na*YesH2O2Na*YesDME3Na*YesDME1Na*YesDME2Na*YesDME2Na*YesDME3K*YesH2O1K*YesH2O2K*YesH2O2K*YesH2O2K*YesDME3Nme4*YesDME3NMe4*YesDME3NMe4*YesH2O2NMe4*YesDME3NMe4*YesDME3NMe4*YesDME3NMe4*YesDME3NMe4*YesDME3NMe4*YesDME3NMe4*YesDME3NMe4*YesDME3NMe4*YesD	None	Yes	H <sub>2</sub> O	3
NoneYesDME2NoneYesDME3Li <sup>+</sup> YesNone0Li <sup>+</sup> YesH2O1Li <sup>+</sup> YesH2O2Li <sup>+</sup> YesDME1Li <sup>+</sup> YesDME2Li <sup>+</sup> YesDME2Li <sup>+</sup> YesDME2Li <sup>+</sup> YesDME3Na <sup>+</sup> YesH2O1Na <sup>+</sup> YesH2O2Na <sup>+</sup> YesH2O2Na <sup>+</sup> YesH2O2Na <sup>+</sup> YesDME1Na <sup>+</sup> YesDME3Na <sup>+</sup> YesDME3K <sup>+</sup> YesDME3K <sup>+</sup> YesDME3K <sup>+</sup> YesH2O1K <sup>+</sup> YesH2O2K <sup>+</sup> YesH2O2K <sup>+</sup> YesDME3K <sup>+</sup> YesDME3Neta <sup>+</sup> YesDME3NMe4 <sup>+</sup> YesH2O3NMe4 <sup>+</sup> YesH2O3NMe4 <sup>+</sup> YesDME3NMe4 <sup>+</sup> YesDME3NMe4 <sup>+</sup> YesDME3NMe4 <sup>+</sup> YesDME3NMe4 <sup>+</sup> YesDME3NMe4 <sup>+</sup> YesDME1NMe4 <sup>+</sup> YesH2O2NMe4 <sup>+</sup> YesH2O3NMe4 <sup>+</sup> Yes<	None	Yes	DME	1
None         Yes         DME         3           Li <sup>+</sup> Yes         None         0           Li <sup>+</sup> Yes         H2O         1           Li <sup>+</sup> Yes         H2O         2           Li <sup>+</sup> Yes         H2O         3           Li <sup>+</sup> Yes         DME         1           Li <sup>+</sup> Yes         DME         3           Li <sup>+</sup> Yes         DME         3           Na <sup>+</sup> Yes         DME         3           Na <sup>+</sup> Yes         Mone         0           Na <sup>+</sup> Yes         DME         1           Na <sup>+</sup> Yes         DME         3           Ka <sup>+</sup> Yes         DME         3           K <sup>+</sup> Yes         DME         3 </td <td>None</td> <td>Yes</td> <td>DME</td> <td>2</td>	None	Yes	DME	2
Li <sup>+</sup> Yes       None       0         Li <sup>+</sup> Yes       H2O       1         Li <sup>+</sup> Yes       H2O       2         Li <sup>+</sup> Yes       DME       1         Li <sup>+</sup> Yes       DME       1         Li <sup>+</sup> Yes       DME       2         Li <sup>+</sup> Yes       DME       3         Na <sup>+</sup> Yes       Mather       0         Na <sup>+</sup> Yes       H2O       2         Na <sup>+</sup> Yes       H2O       2         Na <sup>+</sup> Yes       H2O       2         Na <sup>+</sup> Yes       H2O       3         Na <sup>+</sup> Yes       DME       1         Na <sup>+</sup> Yes       DME       2         Na <sup>+</sup> Yes       DME       3         K <sup>+</sup> Yes       DME       3         K <sup>+</sup> Yes       DME       3         K <sup>+</sup> Yes       H2O       2         K <sup>+</sup> Yes       DME       3         K <sup>+</sup> Yes       DME       3         K <sup>+</sup> Yes       DME       3         NMe4 <sup>+</sup> <t< td=""><td>None</td><td>Yes</td><td>DME</td><td>3</td></t<>	None	Yes	DME	3
Li <sup>+</sup> Yes       H2O       1         Li <sup>+</sup> Yes       H2O       2         Li <sup>+</sup> Yes       DME       1         Li <sup>+</sup> Yes       DME       2         Li <sup>+</sup> Yes       DME       2         Li <sup>+</sup> Yes       DME       2         Li <sup>+</sup> Yes       DME       3         Na <sup>+</sup> Yes       DME       3         Na <sup>+</sup> Yes       H2O       1         Na <sup>+</sup> Yes       H2O       2         Na <sup>+</sup> Yes       H2O       3         Na <sup>+</sup> Yes       DME       3         Na <sup>+</sup> Yes       DME       3         Na <sup>+</sup> Yes       DME       3         K <sup>+</sup> Yes       DME       3         K <sup>+</sup> Yes       DME       3         K <sup>+</sup> Yes       H2O       1         K <sup>+</sup> Yes       DME       3         K <sup>+</sup> Yes       DME       3         K <sup>+</sup> Yes       DME       3         NMe4 <sup>+</sup> Yes       H2O       2         NMe4 <sup>+</sup>	Li <sup>+</sup>	Yes	None	0
Li <sup>+</sup> Yes       H2O       2         Li <sup>+</sup> Yes       DME       1         Li <sup>+</sup> Yes       DME       2         Li <sup>+</sup> Yes       DME       3         Li <sup>+</sup> Yes       DME       3         Na <sup>+</sup> Yes       DME       3         Na <sup>+</sup> Yes       H2O       1         Na <sup>+</sup> Yes       H2O       2         Na <sup>+</sup> Yes       H2O       3         Na <sup>+</sup> Yes       H2O       3         Na <sup>+</sup> Yes       DME       1         Na <sup>+</sup> Yes       DME       1         Na <sup>+</sup> Yes       DME       3         Na <sup>+</sup> Yes       DME       3         Ka <sup>+</sup> Yes       DME       3         K <sup>+</sup> Yes       H2O       1         K <sup>+</sup> Yes       DME       3         K <sup>+</sup> Yes       DME       3         NMe4 <sup>+</sup> Yes       DME       3         NMe4 <sup>+</sup> Yes       DME       1         NMe4 <sup>+</sup> Yes       DME       3         NMe4 <sup>+</sup>	Li <sup>+</sup>	Yes	H <sub>2</sub> O	1
Li <sup>+</sup> Yes       H <sub>2</sub> O       3         Li <sup>+</sup> Yes       DME       1         Li <sup>+</sup> Yes       DME       2         Li <sup>+</sup> Yes       DME       3         Na <sup>+</sup> Yes       DME       3         Na <sup>+</sup> Yes       H <sub>2</sub> O       1         Na <sup>+</sup> Yes       H <sub>2</sub> O       2         Na <sup>+</sup> Yes       H <sub>2</sub> O       3         Na <sup>+</sup> Yes       DME       1         Na <sup>+</sup> Yes       DME       1         Na <sup>+</sup> Yes       DME       2         Na <sup>+</sup> Yes       DME       2         Na <sup>+</sup> Yes       DME       3         K <sup>+</sup> Yes       DME       3         K <sup>+</sup> Yes       DME       3         K <sup>+</sup> Yes       H <sub>2</sub> O       1         K <sup>+</sup> Yes       DME       1         K <sup>+</sup> Yes       DME       3         NMe4 <sup>+</sup> <	Li <sup>+</sup>	Yes	H <sub>2</sub> O	2
Li <sup>+</sup> Yes       DME       1         Li <sup>+</sup> Yes       DME       2         Li <sup>+</sup> Yes       DME       3         Na <sup>+</sup> Yes       None       0         Na <sup>+</sup> Yes       H2O       1         Na <sup>+</sup> Yes       H2O       2         Na <sup>+</sup> Yes       H2O       3         Na <sup>+</sup> Yes       DME       1         Na <sup>+</sup> Yes       DME       1         Na <sup>+</sup> Yes       DME       2         Na <sup>+</sup> Yes       DME       3         Na <sup>+</sup> Yes       DME       3         Ki       Yes       DME       3         K <sup>+</sup> Yes       DME       3         K <sup>+</sup> Yes       H2O       1         K <sup>+</sup> Yes       DME       1         K <sup>+</sup> Yes       DME       1         K <sup>+</sup> Yes       DME       3         NMe4 <sup>+</sup> Yes       DME       1         NMe4 <sup>+</sup> Yes       DME       3         NMe4 <sup>+</sup> Yes       DME       3         NMe4 <sup>+</sup> <	Li <sup>+</sup>	Yes	H <sub>2</sub> O	3
Li <sup>+</sup> Yes       DME       2         Li <sup>+</sup> Yes       DME       3         Na <sup>+</sup> Yes       DME       3         Na <sup>+</sup> Yes       H2O       1         Na <sup>+</sup> Yes       H2O       2         Na <sup>+</sup> Yes       H2O       3         Na <sup>+</sup> Yes       DME       1         Na <sup>+</sup> Yes       DME       2         Na <sup>+</sup> Yes       DME       1         Na <sup>+</sup> Yes       DME       2         Na <sup>+</sup> Yes       DME       3         Na <sup>+</sup> Yes       DME       3         Ka <sup>+</sup> Yes       DME       3         K <sup>+</sup> Yes       H2O       2         K <sup>+</sup> Yes       H2O       3         K <sup>+</sup> Yes       DME       1         K <sup>+</sup> Yes       DME       1         K <sup>+</sup> Yes       DME       3         NMe4 <sup>+</sup> Yes       DME       2         NMe4 <sup>+</sup> Yes       DME       3         NMe4 <sup>+</sup> Yes       DME       3         NEta <sup>+</sup>	Li <sup>+</sup>	Yes	DME	1
$Li^+$ Yes       DME       3         Na <sup>+</sup> Yes       None       0         Na <sup>+</sup> Yes       H2O       1         Na <sup>+</sup> Yes       H2O       2         Na <sup>+</sup> Yes       H2O       3         Na <sup>+</sup> Yes       DME       1         Na <sup>+</sup> Yes       DME       1         Na <sup>+</sup> Yes       DME       2         Na <sup>+</sup> Yes       DME       2         Na <sup>+</sup> Yes       DME       2         Na <sup>+</sup> Yes       DME       3         K <sup>+</sup> Yes       DME       3         K <sup>+</sup> Yes       DME       3         K <sup>+</sup> Yes       H2O       2         K <sup>+</sup> Yes       DME       1         K <sup>+</sup> Yes       DME       1         K <sup>+</sup> Yes       DME       3         NMe4 <sup>+</sup> Yes       DME       1         NMe4 <sup>+</sup> Yes       DME       3         NMe4 <sup>+</sup> Yes       DME       3         NEta <sup>+</sup> Yes       DME       3         NEta <sup>+</sup>	Li <sup>+</sup>	Yes	DME	2
$Na^+$ Yes       None       0 $Na^+$ Yes $H_2O$ 1 $Na^+$ Yes $H_2O$ 2 $Na^+$ Yes $H_2O$ 3 $Na^+$ Yes $DME$ 1 $Na^+$ Yes $DME$ 1 $Na^+$ Yes $DME$ 2 $Na^+$ Yes $DME$ 3 $Na^+$ Yes $DME$ 3 $Na^+$ Yes $DME$ 3 $Na^+$ Yes $None$ 0 $Na^+$ Yes $None$ 0 $K^+$ Yes $None$ 0 $K^+$ Yes $DME$ 1 $K^+$ Yes $DME$ 3 $NMe4^+$ Yes $None$ 0 $NMe4^+$ Yes $DME$ 1 $NMe4^+$ Yes $DME$ 3 $NMe4^+$ Yes $DME$ 3 $NMe4^+$ Yes $DME$ 3 $NMe4^+$ Yes <t< td=""><td>Li<sup>+</sup></td><td>Yes</td><td>DME</td><td>3</td></t<>	Li <sup>+</sup>	Yes	DME	3
Na*       Yes       H2O       1         Na*       Yes       H2O       2         Na*       Yes       H2O       3         Na*       Yes       DME       1         Na*       Yes       DME       1         Na*       Yes       DME       2         Na*       Yes       DME       3         K*       Yes       DME       3         K*       Yes       None       0         K*       Yes       H2O       1         K*       Yes       H2O       2         K*       Yes       H2O       2         K*       Yes       DME       1         K*       Yes       DME       3         K*       Yes       DME       3         NMe4*       Yes       DME       3         NMe4*       Yes       DME       1         NMe4*       Yes       DME       3         NMe4*       Yes       DME       3         NMe4*       Yes       DME       3         NEt4*       Yes       DME       3         NEt4*       Yes       None	Na <sup>+</sup>	Yes	None	0
Na <sup>+</sup> Yes       H2O       2         Na <sup>+</sup> Yes       H2O       3         Na <sup>+</sup> Yes       DME       1         Na <sup>+</sup> Yes       DME       2         Na <sup>+</sup> Yes       DME       3         K <sup>+</sup> Yes       None       0         K <sup>+</sup> Yes       H2O       1         K <sup>+</sup> Yes       DME       1         K <sup>+</sup> Yes       DME       1         K <sup>+</sup> Yes       DME       3         NMe4 <sup>+</sup> Yes       DME       3         NMe4 <sup>+</sup> Yes       DME       1         NMe4 <sup>+</sup> Yes       DME       3         NMe4 <sup>+</sup> Yes       DME       3         NMe4 <sup>+</sup> Yes       DME       3         NEt4 <sup>+</sup> Yes       DME       3         NEt4 <sup>+</sup> Yes       H2O       2         NEt4 <sup>+</sup> Yes       DME       1         NEt4 <sup>+</sup>	Na <sup>+</sup>	Yes	H <sub>2</sub> O	ů 1
Na*       Yes       H2O       3         Na*       Yes       DME       1         Na*       Yes       DME       2         Na*       Yes       DME       3         Na*       Yes       None       0         K*       Yes       H2O       1         K*       Yes       DME       1         K*       Yes       DME       3         NMe4*       Yes       DME       3         NMe4*       Yes       H2O       1         NMe4*       Yes       DME       1         NMe4*       Yes       DME       3         NMe4*       Yes       DME       3         NMe4*       Yes       DME       3         NEt4*       Yes       H2O       2         NEt4*       Yes       H2O	Na <sup>+</sup>	Yes	H <sub>2</sub> O	2
Na <sup>+</sup> Yes       DME       1         Na <sup>+</sup> Yes       DME       2         Na <sup>+</sup> Yes       DME       3         K <sup>+</sup> Yes       DME       3         K <sup>+</sup> Yes       Mone       0         K <sup>+</sup> Yes       H <sub>2</sub> O       1         K <sup>+</sup> Yes       H <sub>2</sub> O       2         K <sup>+</sup> Yes       H <sub>2</sub> O       3         K <sup>+</sup> Yes       DME       1         K <sup>+</sup> Yes       DME       1         K <sup>+</sup> Yes       DME       2         K <sup>+</sup> Yes       DME       3         NMe4 <sup>+</sup> Yes       DME       3         NMe4 <sup>+</sup> Yes       H <sub>2</sub> O       1         NMe4 <sup>+</sup> Yes       DME       1         NMe4 <sup>+</sup> Yes       DME       3         NEt4 <sup>+</sup> Yes       H <sub>2</sub> O       1         NEt4 <sup>+</sup> Yes       DME       1 <td< td=""><td>Na<sup>+</sup></td><td>Yes</td><td>H<sub>2</sub>O</td><td>3</td></td<>	Na <sup>+</sup>	Yes	H <sub>2</sub> O	3
Na <sup>+</sup> Yes       DME       2         Na <sup>+</sup> Yes       DME       3         K <sup>+</sup> Yes       None       0         K <sup>+</sup> Yes       H <sub>2</sub> O       1         K <sup>+</sup> Yes       DME       1         K <sup>+</sup> Yes       DME       1         K <sup>+</sup> Yes       DME       3         NMe <sup>+</sup> Yes       DME       3         NMe4 <sup>+</sup> Yes       None       0         NMe4 <sup>+</sup> Yes       H <sub>2</sub> O       3         NMe4 <sup>+</sup> Yes       DME       1         NMe4 <sup>+</sup> Yes       DME       1         NMe4 <sup>+</sup> Yes       DME       3         NMe4 <sup>+</sup> Yes       DME       3         NEt4 <sup>+</sup> Yes       DME       3         NEt4 <sup>+</sup> Yes       H <sub>2</sub> O       1         NEt4 <sup>+</sup> Yes       H <sub>2</sub> O       2         NEt4 <sup>+</sup> Yes       DME       1	Na <sup>+</sup>	Yes	DME	1
Na <sup>+</sup> Yes       DME       3         Na <sup>+</sup> Yes       DME       3         K <sup>+</sup> Yes       None       0         K <sup>+</sup> Yes       H2O       1         K <sup>+</sup> Yes       H2O       2         K <sup>+</sup> Yes       H2O       3         K <sup>+</sup> Yes       DME       1         K <sup>+</sup> Yes       DME       1         K <sup>+</sup> Yes       DME       3         NMe4 <sup>+</sup> Yes       DME       3         NMe4 <sup>+</sup> Yes       H2O       1         NMe4 <sup>+</sup> Yes       H2O       2         NMe4 <sup>+</sup> Yes       H2O       2         NMe4 <sup>+</sup> Yes       DME       1         NMe4 <sup>+</sup> Yes       DME       3         NMe4 <sup>+</sup> Yes       DME       3         NEt4 <sup>+</sup> Yes       DME       3         NEt4 <sup>+</sup> Yes       H2O       1         NEt4 <sup>+</sup> Yes       H2O       2         NEt4 <sup>+</sup> Yes       H2O       2         NEt4 <sup>+</sup> Yes       DME       1         N	Na <sup>+</sup>	Yes	DME	2
Num       Yes       None       0 $K^+$ Yes       H <sub>2</sub> O       1 $K^+$ Yes       H <sub>2</sub> O       2 $K^+$ Yes       H <sub>2</sub> O       3 $K^+$ Yes       DME       1 $K^+$ Yes       DME       1 $K^+$ Yes       DME       2 $K^+$ Yes       DME       3         NMe4 <sup>+</sup> Yes       DME       3         NMe4 <sup>+</sup> Yes       H <sub>2</sub> O       2         NMe4 <sup>+</sup> Yes       H <sub>2</sub> O       2         NMe4 <sup>+</sup> Yes       DME       1         NMe4 <sup>+</sup> Yes       DME       1         NMe4 <sup>+</sup> Yes       DME       2         NMe4 <sup>+</sup> Yes       DME       2         NMe4 <sup>+</sup> Yes       DME       3         NMe4 <sup>+</sup> Yes       DME       3         NMe4 <sup>+</sup> Yes       DME       2         NMe4 <sup>+</sup> Yes       H <sub>2</sub> O       1         NMe4 <sup>+</sup> Yes       DME       3         NEt4 <sup>+</sup> Yes       DME       1	Na <sup>+</sup>	Yes	DME	3
$K^+$ Yes       H2O       1 $K^+$ Yes       H2O       2 $K^+$ Yes       DME       1 $K^+$ Yes       DME       2 $K^+$ Yes       DME       3         NMe4 <sup>+</sup> Yes       DME       3         NMe4 <sup>+</sup> Yes       H2O       1         NMe4 <sup>+</sup> Yes       DME       3         NMe4 <sup>+</sup> Yes       H2O       1         NMe4 <sup>+</sup> Yes       DME       3         NMe4 <sup>+</sup> Yes       DME       1         NMe4 <sup>+</sup> Yes       DME       1         NMe4 <sup>+</sup> Yes       DME       3         NEt4 <sup>+</sup> Yes       H2O       2         NEt4 <sup>+</sup> Yes       DME       1         NEt4 <sup>+</sup> Yes       DME       1         NEt4 <sup>+</sup> Yes       DME       3 <t< td=""><td>K<sup>+</sup></td><td>Yes</td><td>None</td><td>0</td></t<>	K <sup>+</sup>	Yes	None	0
$K^+$ Yes       H2O       2 $K^+$ Yes       H2O       3 $K^+$ Yes       DME       1 $K^+$ Yes       DME       2 $K^+$ Yes       DME       3         NMe4 <sup>+</sup> Yes       DME       3         NMe4 <sup>+</sup> Yes       H2O       1         NMe4 <sup>+</sup> Yes       H2O       1         NMe4 <sup>+</sup> Yes       H2O       2         NMe4 <sup>+</sup> Yes       H2O       1         NMe4 <sup>+</sup> Yes       H2O       2         NMe4 <sup>+</sup> Yes       DME       1         NMe4 <sup>+</sup> Yes       DME       1         NMe4 <sup>+</sup> Yes       DME       3         NEta <sup>+</sup> Yes       DME       3         NEta <sup>+</sup> Yes       H2O       1         NEta <sup>+</sup> Yes       H2O       2         NEta <sup>+</sup> Yes       DME       1         NEta <sup>+</sup> Yes       DME       1         NEta <sup>+</sup> Yes       DME       3         NPra <sup>+</sup> Yes       DME       3 <td>K<sup>+</sup></td> <td>Yes</td> <td>H<sub>2</sub>O</td> <td>ů 1</td>	K <sup>+</sup>	Yes	H <sub>2</sub> O	ů 1
$K^+$ Yes       H2O       3 $K^+$ Yes       DME       1 $K^+$ Yes       DME       2 $K^+$ Yes       DME       3         NMe4 <sup>+</sup> Yes       DME       3         NMe4 <sup>+</sup> Yes       H2O       1         NMe4 <sup>+</sup> Yes       H2O       1         NMe4 <sup>+</sup> Yes       H2O       2         NMe4 <sup>+</sup> Yes       H2O       3         NMe4 <sup>+</sup> Yes       DME       1         NMe4 <sup>+</sup> Yes       DME       2         NMe4 <sup>+</sup> Yes       DME       1         NMe4 <sup>+</sup> Yes       DME       3         NEt4 <sup>+</sup> Yes       DME       3         NEt4 <sup>+</sup> Yes       H2O       1         NEt4 <sup>+</sup> Yes       H2O       2         NEt4 <sup>+</sup> Yes       DME       1         NEt4 <sup>+</sup> Yes       DME       1         NEt4 <sup>+</sup> Yes       DME       3         NEt4 <sup>+</sup> Yes       DME       3         NPr4 <sup>+</sup> Yes       DME       3 </td <td>K<sup>+</sup></td> <td>Yes</td> <td>H<sub>2</sub>O</td> <td>2</td>	K <sup>+</sup>	Yes	H <sub>2</sub> O	2
$K^+$ Yes       DME       1 $K^+$ Yes       DME       2 $K^+$ Yes       DME       3         NMe4 <sup>+</sup> Yes       None       0         NMe4 <sup>+</sup> Yes       H2O       1         NMe4 <sup>+</sup> Yes       H2O       2         NMe4 <sup>+</sup> Yes       H2O       3         NMe4 <sup>+</sup> Yes       DME       1         NMe4 <sup>+</sup> Yes       DME       2         NMe4 <sup>+</sup> Yes       DME       3         NMe4 <sup>+</sup> Yes       None       0         NEta <sup>+</sup> Yes       None       0         NEta <sup>+</sup> Yes       H2O       1         NEta <sup>+</sup> Yes       DME       1         NEta <sup>+</sup> Yes       DME       1         NEta <sup>+</sup> Yes       DME       2         NEta <sup>+</sup> Yes       DME       3         NEta <sup>+</sup> Yes       DME       3	K K <sup>+</sup>	Yes	H <sub>2</sub> O	3
$K^+$ YesDME2 $K^+$ YesDME3 $NMe4^+$ YesNone0 $NMe4^+$ YesH2O1 $NMe4^+$ YesH2O2 $NMe4^+$ YesH2O3 $NMe4^+$ YesDME1 $NMe4^+$ YesDME1 $NMe4^+$ YesDME2 $NMe4^+$ YesDME3 $NMe4^+$ YesDME3 $NEt4^+$ YesNone0 $NEt4^+$ YesH2O1 $NEt4^+$ YesH2O2 $NEt4^+$ YesDME1 $NEt4^+$ YesDME1 $NEt4^+$ YesDME1 $NEt4^+$ YesDME3 $NEt4^+$ YesNone0	K K <sup>+</sup>	Yes	DME	1
$K^+$ Yes       DME       3         NMe4 <sup>+</sup> Yes       None       0         NMe4 <sup>+</sup> Yes       H <sub>2</sub> O       1         NMe4 <sup>+</sup> Yes       H <sub>2</sub> O       2         NMe4 <sup>+</sup> Yes       H <sub>2</sub> O       3         NMe4 <sup>+</sup> Yes       DME       1         NMe4 <sup>+</sup> Yes       DME       1         NMe4 <sup>+</sup> Yes       DME       2         NMe4 <sup>+</sup> Yes       DME       3         NEt4 <sup>+</sup> Yes       None       0         NEt4 <sup>+</sup> Yes       H <sub>2</sub> O       1         NEt4 <sup>+</sup> Yes       H <sub>2</sub> O       2         NEt4 <sup>+</sup> Yes       DME       1         NEt4 <sup>+</sup> Yes       DME       1         NEt4 <sup>+</sup> Yes       DME       2         NEt4 <sup>+</sup> Yes       DME       3         NEt4 <sup>+</sup> Yes       DME       3         NEt4 <sup>+</sup> Yes       None       0<	K K <sup>+</sup>	Yes	DME	2
N       Fes       DARE       S         NMe4 <sup>+</sup> Yes       None       0         NMe4 <sup>+</sup> Yes       H <sub>2</sub> O       1         NMe4 <sup>+</sup> Yes       H <sub>2</sub> O       2         NMe4 <sup>+</sup> Yes       DME       1         NMe4 <sup>+</sup> Yes       DME       1         NMe4 <sup>+</sup> Yes       DME       2         NMe4 <sup>+</sup> Yes       DME       2         NMe4 <sup>+</sup> Yes       DME       3         NEt4 <sup>+</sup> Yes       None       0         NEt4 <sup>+</sup> Yes       H <sub>2</sub> O       1         NEt4 <sup>+</sup> Yes       H <sub>2</sub> O       1         NEt4 <sup>+</sup> Yes       H <sub>2</sub> O       1         NEt4 <sup>+</sup> Yes       H <sub>2</sub> O       2         NEt4 <sup>+</sup> Yes       H <sub>2</sub> O       3         NEt4 <sup>+</sup> Yes       DME       1         NEt4 <sup>+</sup> Yes       DME       1         NEt4 <sup>+</sup> Yes       DME       3         NEt4 <sup>+</sup> Yes       DME       3         NEt4 <sup>+</sup> Yes       DME       3         NPr4 <sup>+</sup> Yes       None       0	K <sup>+</sup>	Yes	DME	3
NMe4 <sup>+</sup> Yes       H2O       1         NMe4 <sup>+</sup> Yes       H2O       2         NMe4 <sup>+</sup> Yes       H2O       3         NMe4 <sup>+</sup> Yes       DME       1         NMe4 <sup>+</sup> Yes       DME       1         NMe4 <sup>+</sup> Yes       DME       2         NMe4 <sup>+</sup> Yes       DME       3         NMe4 <sup>+</sup> Yes       DME       3         NMe4 <sup>+</sup> Yes       None       0         NEt4 <sup>+</sup> Yes       None       0         NEt4 <sup>+</sup> Yes       H2O       1         NEt4 <sup>+</sup> Yes       H2O       1         NEt4 <sup>+</sup> Yes       H2O       2         NEt4 <sup>+</sup> Yes       H2O       3         NEt4 <sup>+</sup> Yes       DME       1         NEt4 <sup>+</sup> Yes       DME       1         NEt4 <sup>+</sup> Yes       DME       3         NEt4 <sup>+</sup> Yes       DME       3         NEt4 <sup>+</sup> Yes       DME       3         NPr4 <sup>+</sup> Yes       None       0	NMe <sup>4+</sup>	Yes	None	0
NMe4 <sup>+</sup> Yes $H_2O$ 2         NMe4 <sup>+</sup> Yes $H_2O$ 3         NMe4 <sup>+</sup> Yes       DME       1         NMe4 <sup>+</sup> Yes       DME       2         NMe4 <sup>+</sup> Yes       DME       3         NMe4 <sup>+</sup> Yes       DME       3         NMe4 <sup>+</sup> Yes       DME       3         NEt4 <sup>+</sup> Yes       None       0         NEt4 <sup>+</sup> Yes       H2O       1         NEt4 <sup>+</sup> Yes       H2O       2         NEt4 <sup>+</sup> Yes       H2O       1         NEt4 <sup>+</sup> Yes       H2O       3         NEt4 <sup>+</sup> Yes       H2O       3         NEt4 <sup>+</sup> Yes       DME       1         NEt4 <sup>+</sup> Yes       DME       1         NEt4 <sup>+</sup> Yes       DME       2         NEt4 <sup>+</sup> Yes       DME       3         NPr4 <sup>+</sup> Yes       None       0	NMe <sub>4</sub> <sup>+</sup>	Yes	H <sub>2</sub> O	1
NMe4+YesH2O2NMe4+YesDME1NMe4+YesDME2NMe4+YesDME3NEt4+YesNone0NEt4+YesH2O1NEt4+YesH2O2NEt4+YesH2O3NEt4+YesH2O2NEt4+YesH2O3NEt4+YesDME1NEt4+YesDME1NEt4+YesDME1NEt4+YesDME3NEt4+YesDME3NEt4+YesDME3NEt4+YesDME3NEt4+YesDME3NPr4+YesNone0	NMe <sub>4</sub> <sup>+</sup>	Yes	H <sub>2</sub> O	2
NMe4+YesDME1 $NMe4^+$ YesDME2 $NMe4^+$ YesDME3 $NEt4^+$ YesNone0 $NEt4^+$ YesH2O1 $NEt4^+$ YesH2O2 $NEt4^+$ YesH2O3 $NEt4^+$ YesDME1 $NEt4^+$ YesDME1 $NEt4^+$ YesDME3 $NEt4^+$ YesDME3 $NEt4^+$ YesDME3 $NEt4^+$ YesDME3 $NEt4^+$ YesDME3 $NPr4^+$ YesNone0	NMe <sub>4</sub> <sup>+</sup>	Yes	H <sub>2</sub> O	3
NMe4+ NMe4+YesDME2NMe4+ YesYesDME3NEt4+ NEt4+YesNone0NEt4+ NEt4+YesH2O1NEt4+ YesYesH2O2NEt4+ NEt4+YesDME1NEt4+ NEt4+YesDME1NEt4+ NEt4+YesDME2NEt4+ NEt4+YesDME3NEt4+ NEt4+YesDME3NEt4+ NEt4+YesDME3NPt4+ YesYesNone0	NMe <sub>4</sub> <sup>+</sup>	Yes	DME	1
NMe4+YesDME2 $NMe4^+$ YesDME3 $NEt4^+$ YesNone0 $NEt4^+$ YesH2O1 $NEt4^+$ YesH2O2 $NEt4^+$ YesDME1 $NEt4^+$ YesDME1 $NEt4^+$ YesDME2 $NEt4^+$ YesDME3 $NEt4^+$ YesDME3 $NEt4^+$ YesDME3 $NEt4^+$ YesDME0	NMe <sub>4</sub> <sup>+</sup>	Yes	DME	2
NHICH NEta+YesDAL $\beta$ NEta+YesNone0NEta+YesH2O1NEta+YesH2O2NEta+YesDME1NEta+YesDME1NEta+YesDME2NEta+YesDME3NEta+YesDME3NEta+YesDME3NEta+YesNone0	NMe <sub>4</sub> <sup>+</sup>	Yes	DME	3
NEt4+YesH2O1NEt4+YesH2O2NEt4+YesH2O3NEt4+YesDME1NEt4+YesDME2NEt4+YesDME3NEt4+YesDME3NEt4+YesDME0	NEt <sup>4</sup>	Yes	None	0
NEta+YesH2O2NEta+YesH2O3NEta+YesDME1NEta+YesDME2NEta+YesDME3NEta+YesDME3NPra+YesNone0	NEt <sup>4</sup>	Yes	H <sub>2</sub> O	0 1
NEta+Yes $H_2O$ 3NEta+YesDME1NEta+YesDME2NEta+YesDME3NPra+YesNone0	NEt <sub>4</sub> <sup>+</sup>	Yes	H <sub>2</sub> O	2
NEta+YesDME1NEta+YesDME2NEta+YesDME3NPra+YesNone0	NEt <sup>4</sup>	Yes	H <sub>2</sub> O	3
NEt4+YesDME2NEt4+YesDME3NPr4+YesNone0	NEt <sup>4</sup>	Yes	DME	1
NEt4+YesDME2NPr4+YesNone0	NEt <sup>4</sup>	Yes	DME	2
NPr4 <sup>+</sup> Yes None 0	NEt <sup>4</sup>	Yes	DME	- 3
	NPr4 <sup>+</sup>	Yes	None	0

C. Table S1: List of systems simulated using ADMP.

$NPr_4^+$	Yes	H <sub>2</sub> O	1
$NPr_4^+$	Yes	H <sub>2</sub> O	2
$NPr_4^+$	Yes	H <sub>2</sub> O	3
$NPr_4^+$	Yes	DME	1
$NPr_4^+$	Yes	DME	2
$NPr_4^+$	Yes	DME	3
$NBu_4^+$	Yes	None	0
$NBu_4^+$	Yes	H <sub>2</sub> O	1
$NBu_4^+$	Yes	H <sub>2</sub> O	2
$NBu_4^+$	Yes	H <sub>2</sub> O	3
$NBu_4^+$	Yes	H <sub>2</sub> O	3 + implicit solvent
$NBu_4^+$	Yes	DME	1
$NBu_4^+$	Yes	DME	2
$NBu_4^+$	Yes	DME	3
$NBu_4^+$	Yes	DME	3 + implicit solvent
$NBu_4^+$	Yes	THF	3 + implicit solvent
$NBu_4^+$	Yes	DMSO	3 + implicit solvent
$NBu4^+$	Yes	Acetonitrile	3 + implicit solvent
NBu <sub>4</sub> <sup>+</sup>	Yes	DMF	3 + implicit solvent

**D.** DFT-level optimized structures of  $NBu_{4^+}$ 



**Figure S1**: DFT-level optimized structures of  $NBu_4^+$ – $CO_2^-$ –solvent with (a) DME and (b) H<sub>2</sub>O.



**E.** Cation-to-CO<sub>2</sub><sup>-</sup> bond distance trends in various complexes with increasing number of solvent molecules (DME and water)

**Figure S2**: Average and DFT-optimized cation-to- $CO_2^-$  distance for clusters with 0-3 solvent molecules. Lithium is the most sensitive to adding DME molecules, and there is little to no difference from increasing the bond length of the alkyl arms on the ammonium cations after ethyl.

Additional Details: We report up to 3 solvent molecules, based on a desire to ensure that the majority of the explicit monovalent ion-solvent interactions could be accounted for and that a  $Li^+$  first solvation shell typically has four coordination. We also tested up to 5 molecules and observed that the optimized angle remains unchanged with additional solvent molecules (Figure S4). For all cation–CO<sub>2</sub><sup>-</sup>–solvent complexes, except for Li<sup>+</sup>–CO<sub>2</sub><sup>-</sup>–*n*DME, the average angles of CO<sub>2</sub><sup>-</sup> are not sensitive to the number of solvent molecules beyond one solvent molecule (Figure 4 of the main manuscript).

DFT-optimized  $CO_2^-$  bond angle of different cation- $CO_2^-$ -solvent molecular complexes: (left) cation- $CO_2^-$ -DME and (right) cation- $CO_2^-$ -H<sub>2</sub>O



Figure S3: DFT-optimized bond angle of  $CO_2^-$  for complexes with 0-3 DME or H<sub>2</sub>O.



**Figure S4:** DFT-optimized (gas phase)  $CO_2^-$  bond angle with up to 5 water molecules for Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, and NBu4<sup>+</sup> cations.

#### F. A physics-based model

To decompose the DFT-calculated complexation enthalpies into stabilization effects by electrostatic ion-ion interaction, ion-dipole interaction, and dipole-dipole interaction, we have constructed a simple physics-based model. In this model we only consider pairwise interactions (Figure S5) and we sum up all the pairwise interactions to approximate the complexation energy of the system.



**Figure S5:** Schematics of ion-ion, ion-dipole, and dipole-dipole interactions. Adapted with permission from ref 1. Copyright 2011 Elsevier.

The ion-ion interaction is calculated as:

$$Q_1 Q_2 / 4\pi \varepsilon r$$

The ion-dipole interaction is calculated as:

 $-Qu\cos\theta/4\pi\varepsilon r^2$ 

The dipole-dipole interaction is calculated as:

$$-u_1u_2(2\cos\theta_1\cos\theta_2-\sin\theta_1\sin\theta_2\cos\phi)/4\pi\varepsilon r^3$$
,

where Q ( $Q_1$  and  $Q_2$ ) is the charge, u ( $u_1$  and  $u_2$ ) is the dipole moment, r is the separating distance,  $\varepsilon$  is the permittivity,  $\Theta_i$  is the angle between  $u_i$  and r, and  $\varphi$  is the angle between  $u_1$  and  $u_2$ .<sup>1</sup> For H<sub>2</sub>O and DME we used a dipole moment of 2.04 and 1.59 D, respectively. The distances and angles were measured from the optimized geometry of the cluster. The clusters used in this physics-based model were selected from Table S1 with cation = Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, NBu4<sup>+</sup> and solvent = None, H<sub>2</sub>O, DME.



Figure S6: Complexation enthalpy of two clusters of  $Li^+$ – $CO_2^-$ – $4H_2O$  as a function of charge of  $CO_2$ .

## Reference

1. Israelachvili, J.N. Intermolecular and Surface Forces, (Third Edition), Academic Press, 2011