Interactions of CO₂ Anion Radical with Electrolyte Environments from First-Principles Simulations

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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

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

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-cc-pVDZ 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-cc-pVDZ 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 (ΔH)

e.g., for Li^+–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_{CO2-}) is calculated by:

$$BE_{CO_2^-} = H(Li^+, CO_2^-, 3DME) - H(Li^+, 3DME) - H(CO_2^-)$$
$$= \Delta H_{complex}(Li^+, CO_2^-, 3DME) - \Delta H_{complex}(Li^+, 3DME).$$

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

Cation	CO_2^-	Solvent Identity	Number of Solvent Molecules
None	Yes	None	0
None	Yes	H_2O	1
None	Yes	H_2O	2
None	Yes	H_2O	3
None	Yes	DME	1
None	Yes	DME	2
None	Yes	DME	3
Li^+	Yes	None	0
Li^+	Yes	H_2O	1
Li^+	Yes	H_2O	2
Li^+	Yes	H_2O	3
Li^+	Yes	DME	1
Li^+	Yes	DME	2
Li^+	Yes	DME	3
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	2
Na^+	Yes	DME	3
K^+	Yes	None	0
K^+	Yes	H_2O	1
K^+	Yes	H_2O	2
K^+	Yes	H_2O	3
K^+	Yes	DME	1
K^+	Yes	DME	2
K^+	Yes	DME	3
NMe_4^+	Yes	None	0
NMe_4^+	Yes	H_2O	1
NMe_4^+	Yes	H_2O	2
NMe_4^+	Yes	H_2O	3
NMe_4^+	Yes	DME	1
NMe_4^+	Yes	DME	2
NMe_4^+	Yes	DME	3
NEt_4^+	Yes	None	0
NEt_4^+	Yes	H_2O	1
NEt_4^+	Yes	H_2O	2
NEt_4^+	Yes	H_2O	3
NEt_4^+	Yes	DME	1
NEt_4^+	Yes	DME	2
NEt_4^+	Yes	DME	3
NPr_4^+	Yes	None	0

NPr_4^+	Yes	H_2O	1
NPr_4^+	Yes	H_2O	2
NPr_4^+	Yes	H_2O	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_2O	1
NBu_4^+	Yes	H_2O	2
NBu_4^+	Yes	H_2O	3
NBu_4^+	Yes	H_2O	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
NBu_4^+	Yes	Acetonitrile	3 + implicit solvent
NBu_4^+	Yes	DMF	3 + implicit solvent

D. DFT-level optimized structures of NBu_4^+

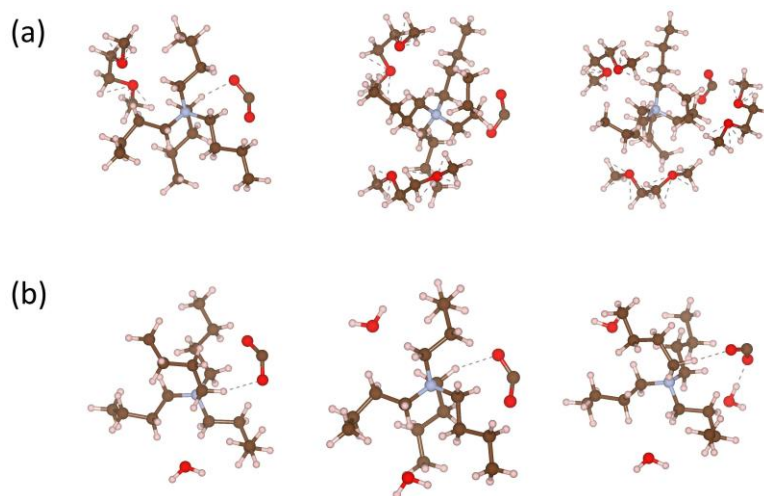**Figure S1**: DFT-level optimized structures of $NBu_4^+–CO_2^-–$solvent with (a) DME and (b) H_2O.

E. Cation-to-CO_2^- bond distance trends in various complexes with increasing number of solvent molecules (DME and water)
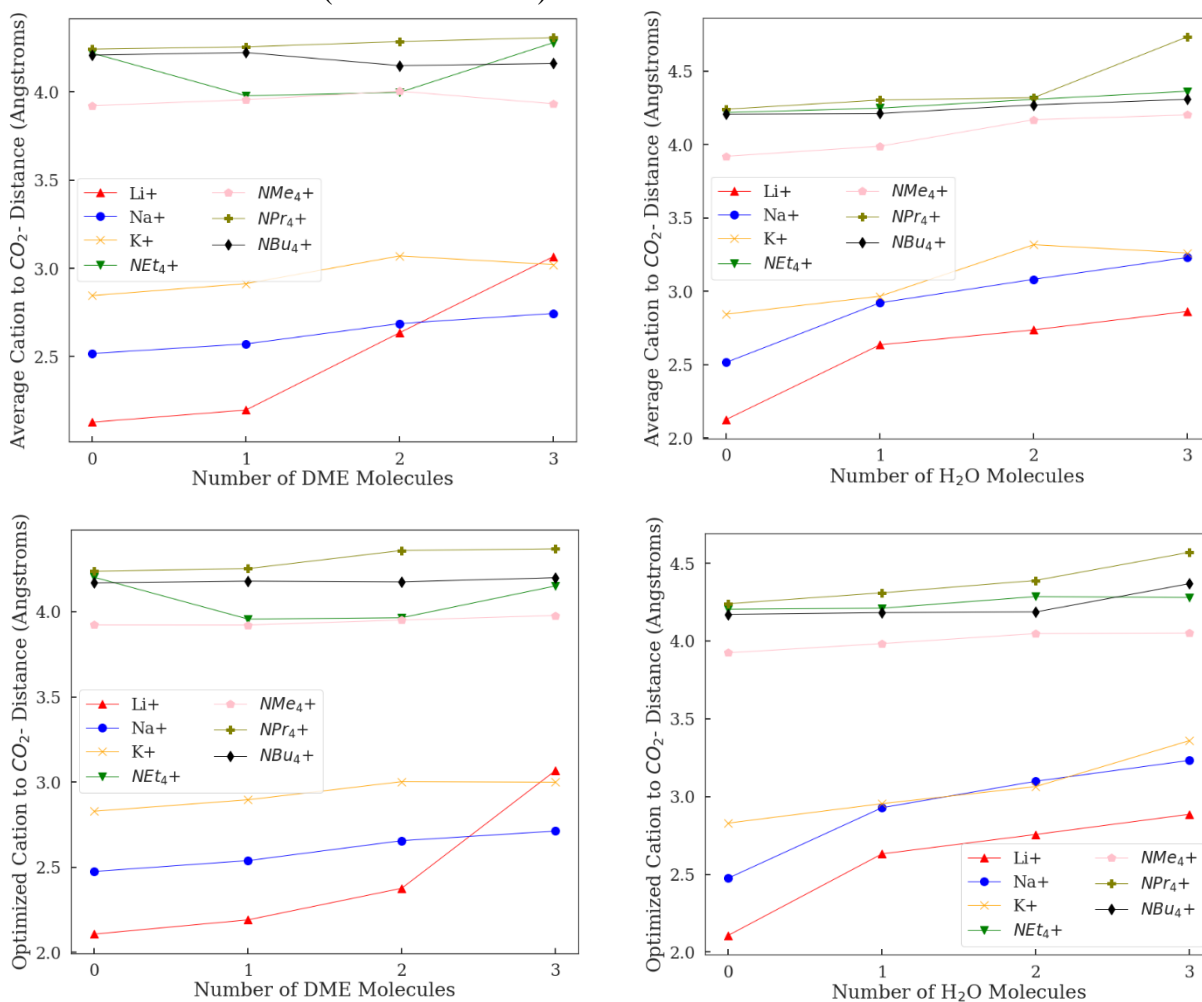

Figure S2: Average and DFT-optimized cation-to-CO_2^- distance for clusters with 0-3 solvent molecules. Lithium is the most sensitive to adding DME molecules, and there is little to no difference from increasing the bond length of the alkyl arms on the ammonium cations after ethyl.

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_2^-–solvent complexes, except for Li^+–CO_2^-–nDME, the average angles of CO_2^- 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_2O
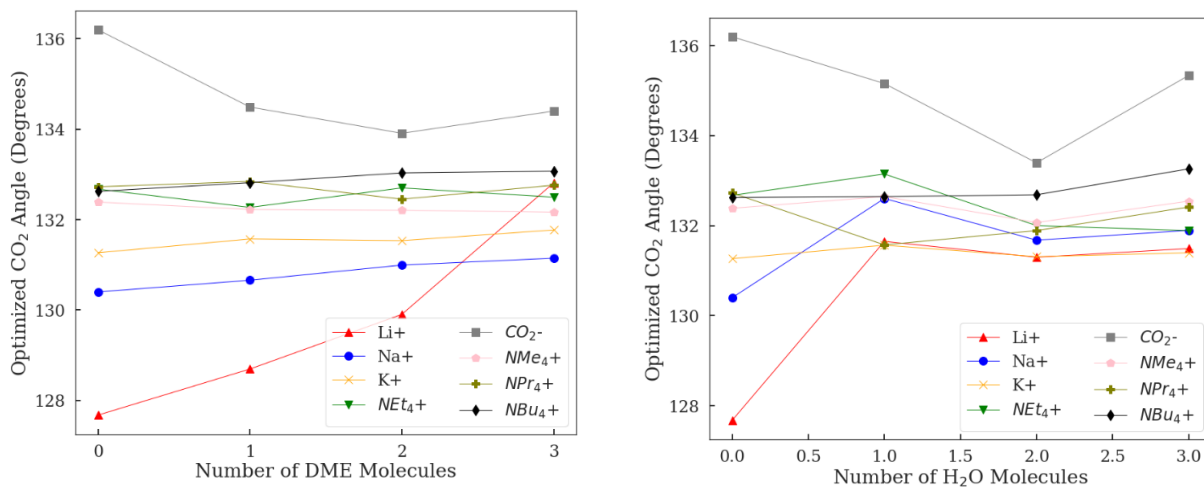

Figure S3: DFT-optimized bond angle of CO_2^- for complexes with 0-3 DME or H_2O.
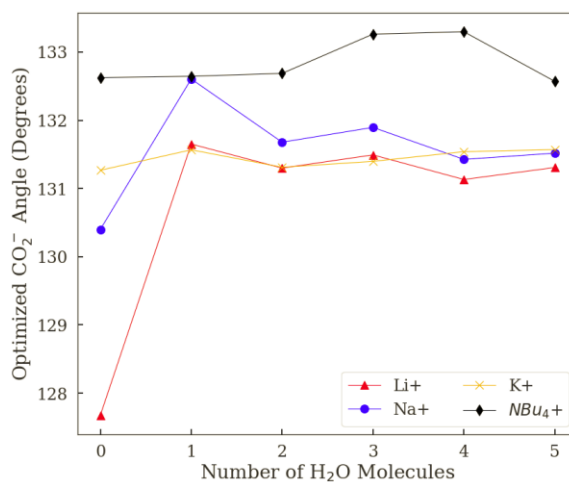

Figure S4: DFT-optimized (gas phase) CO_2^- bond angle with up to 5 water molecules for Li^+, Na^+, K^+, and NBu_4^+ cations.

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.
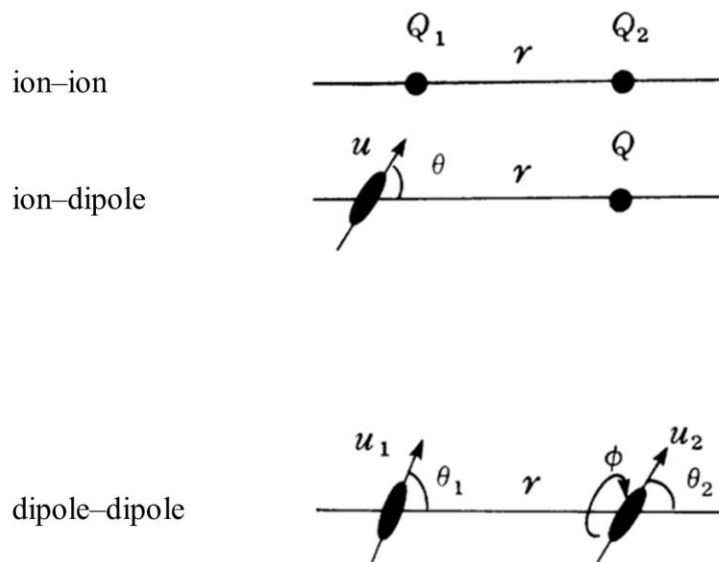

Figure S5: Schematics of ion-ion, ion-dipole, and dipole-dipole interactions. Adapted with permission from ref 1. Copyright 2011 Elsevier.

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:

$$-u_1 u_2 (2\cos\theta_1 \cos\theta_2 - \sin\theta_1 \sin\theta_2 \cos\phi) / 4\pi\varepsilon r^3 ,$$

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, ε is the permittivity, Θ_i is the angle between u_i and r, and φ is the angle between u_1 and u_2.[1] For H_2O 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^+, Na^+, K^+, NBu_4^+ and solvent = None, H_2O, DME.
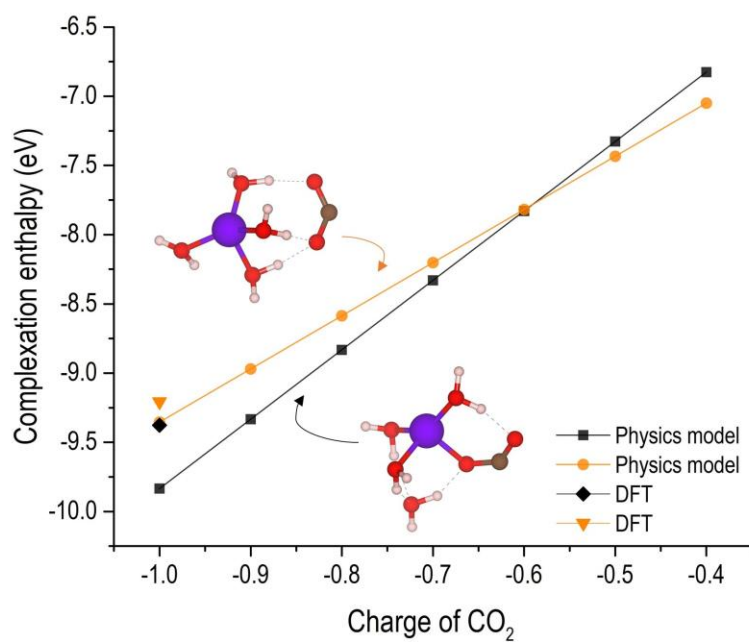
Figure S6: Complexation enthalpy of two clusters of Li^+–CO_2^-–$4H_2O$ as a function of charge of CO_2.

Reference

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