

Abstract & Introduction

Molecular mechanics models in computational chemistry are used to understand the dynamics behind interactions at the molecular level. Ethylene carbonate is one of the most common solvents used for the production of batteries in cars, phones, and laptops. Using the commonly used models GAFF¹ and OPLS,² the dynamics of the ions fluorine, chlorine, bromine, iodine, and potassium in ethylene carbonate are studied to better understand the efficacy of the materials used in battery production. Using known calculated quantum theory values for the dimer energy and geometry between an ion and a single molecule of ethylene carbonate, it was found that both the GAFF and OPLS models were accurate in reproducing solvent-ion interactions. In addition, for the GAFF model, free energy calculations were performed to further validate the model with experimental data. For each of these calculations, the optimal values for sigma and epsilon stayed consistent with trends following the size of the ions. These models with their optimized input values can more accurately simulate the interactions between ethylene carbonate and the given ions, thus leading to better results. A great benefit of using models is being able to predict the outcome of a physical experiment prior to actually performing it, which saves both time and materials.

Methods

GROMACS³ (GROningen Machine for Chemical Substances), a molecular dynamics software package, was used to run simulations. These simulations were run with periodic boundary conditions at constant temperature and constant pressure. GAFF and OPLS models were tested by simulating a single ion with 1000 EC molecules. Dimer energy, geometry, and free energy were then calculated. Ion-EC interactions between atoms *i* and *j* are defined by the Lennard-Jones potential in addition to a Coulombic term:

$$E_{ij}(r_{ij}) = 4\epsilon_{ij} \left[\left(\frac{r_{\downarrow ij}}{\sigma_{\downarrow ij}} \right)^{12} - \left(\frac{r_{\downarrow ij}}{\sigma_{\downarrow ij}} \right)^6 \right] + \frac{q_{\downarrow i} q_{\downarrow j}}{r_{\downarrow ij}}$$

For GAFF, the Lorentz-Berthelot combining rules were used:

$$\epsilon_{ij} = (\epsilon_i \epsilon_j)^{1/2}$$

$$\sigma_{ij} = (\sigma_i + \sigma_j)/2$$

where q_i is the charge of atom *i*. Thermodynamic integration was used to calculate free energy changes between different parameters for each ion.

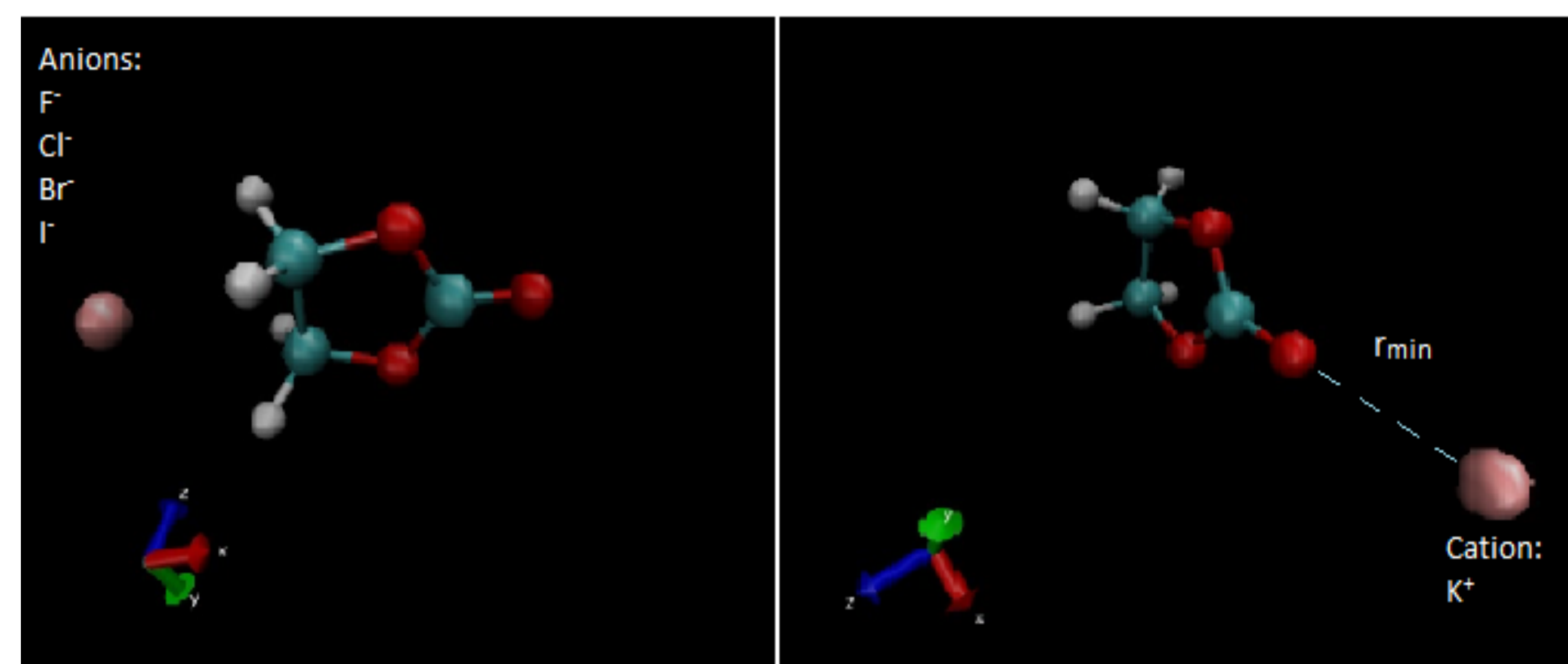
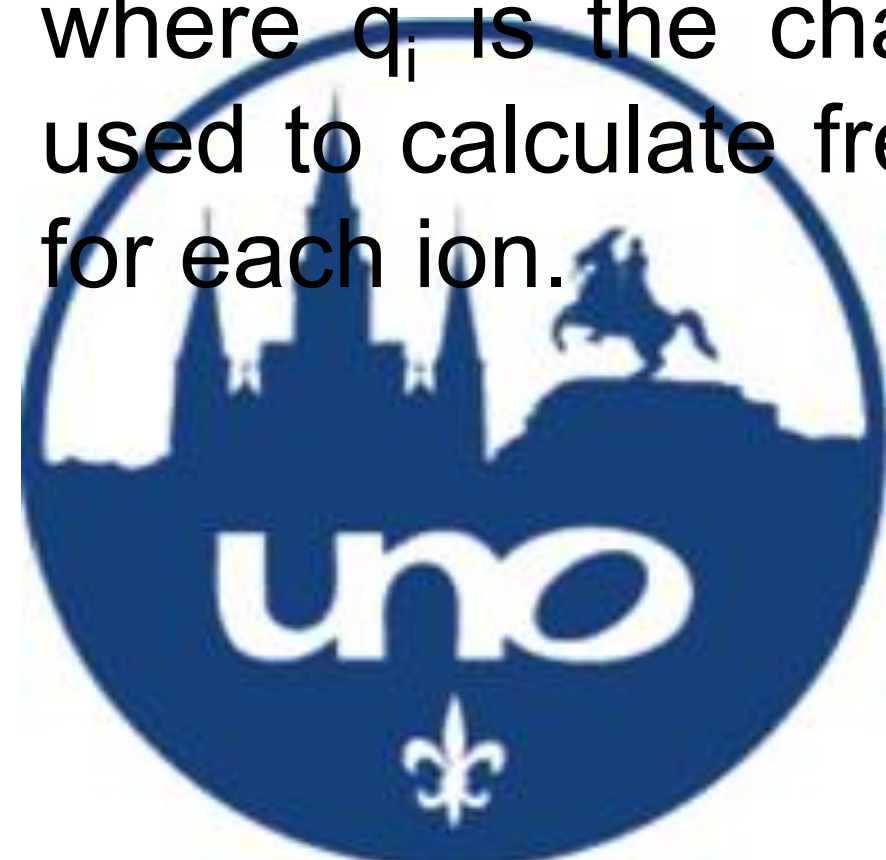


Figure 1: image of a single ethylene carbonate atom with an ion produced by Visual Molecular Dynamics. The red atoms are oxygens, blue atoms are carbons, and silver atoms are hydrogen. The dotted blue line represents r_{\min} , which is the distance from the ion to the carbon furthest from the hydrogens.

Ion	ϵ (kcal/mol)	σ (Å)	Quantum theory values	
			r_{\min} (Å)	E_{\min} (kcal/mol)
F ⁻	0.1038	2.47	5.7946	-32.20
Cl ⁻	0.1276	3.55	6.3942	-22.88
Br ⁻	0.1516	3.9	6.5246	-20.96
I ⁻	0.1576	3.75	6.699	*****
K ⁺	0.05975	2.6	2.51	-28.26

Table 1: optimal values of epsilon and sigma used for GAFF and OPLS models to the left. Quantum theory values for r_{\min} and E_{\min} to the right.

Ion	GAFF model			
	r_{\min} (Å)	% error	E_{\min} (kcal/mol)	% error
F ⁻	5.8454	8.58	-28.17	12.53
Cl ⁻	6.4224	10.84	-21.47	6.17
Br ⁻	6.6238	1.52	-19.72	5.91
I ⁻	6.5571	2.12	-20.37	*****
K ⁺	2.28	9.16	-28.17	0.30

Table 2: values of r_{\min} and E_{\min} for each ion calculated from GAFF with % errors compared to quantum theory values.

Ion	OPLS model			
	r_{\min} (Å)	% error	E_{\min} (kcal/mol)	% error
F ⁻	5.7080	10.73	-28.09	12.75
Cl ⁻	6.3176	9.03	-20.68	9.64
Br ⁻	6.5150	0.15	-19.00	9.36
I ⁻	6.4415	3.84	-19.61	*****
K ⁺	2.30	8.37	-25.91	8.33

Table 3: values of r_{\min} and E_{\min} calculated for each ion from OPLS with % errors compared to quantum theory values.

FREE ENERGY DATA

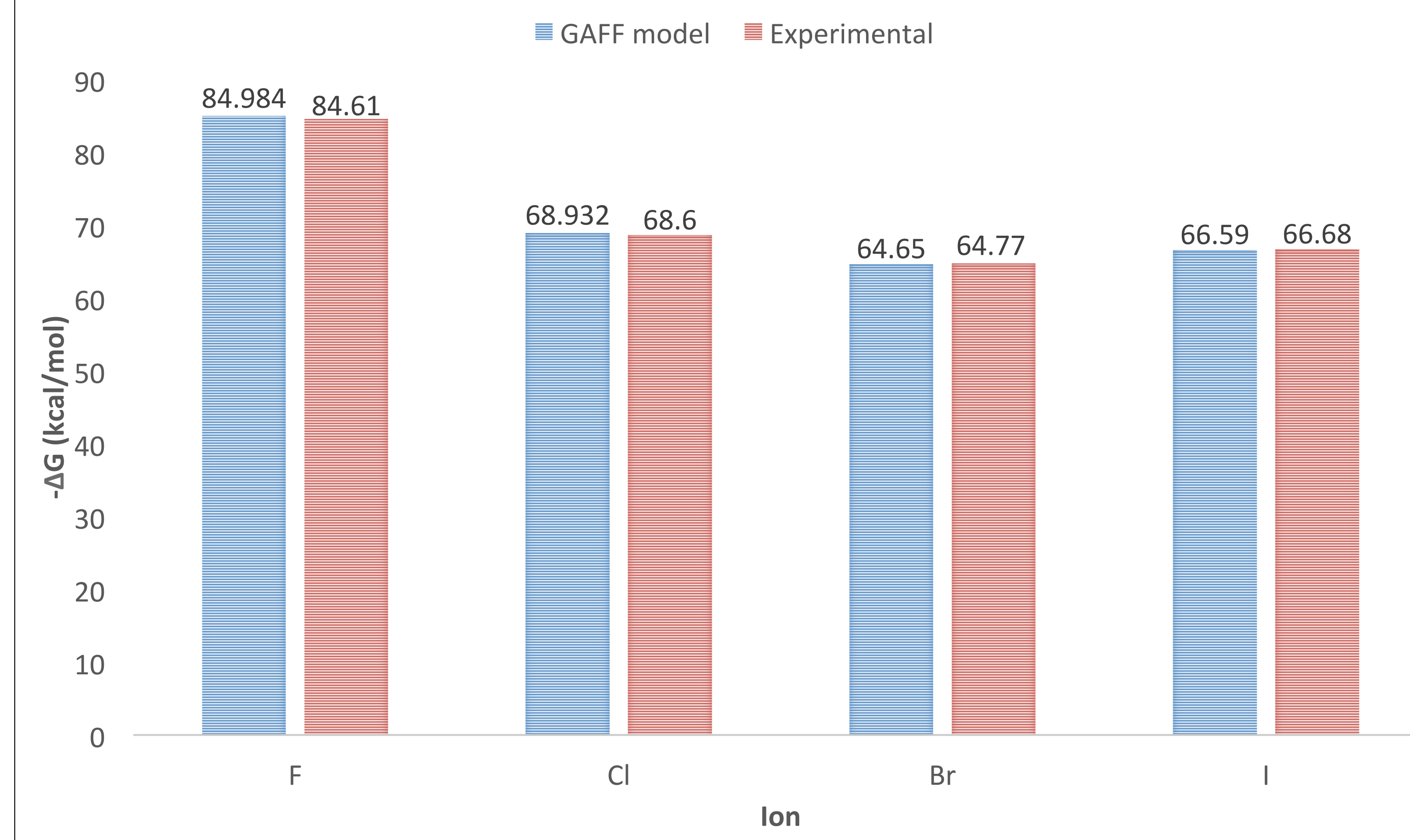


Figure 2: bar graph of free energy calculations from GAFF compared to experimental data⁴.

Results

The values of sigma and epsilon shown in Table 1 were proven to be the optimum parameters for these ions when using GAFF and attempting to match the experimental free energy values found on Figure 2. Using these values also yielded the smallest margin of error for E_{\min} and r_{\min} for both the GAFF and OPLS models. The GAFF model was shown to have less error with regards to E_{\min} while the OPLS model was slightly more accurate in some cases with regards to r_{\min} , as shown in Tables 2 and 3. The free energy values from the GAFF model using these parameters all differ by less than 1kcal/mol when compared to the experimental data, as seen in Figure 2. These more accurate parameters allow future studies to obtain more precise and realistic results when modeling EC with F⁻, Cl⁻, Br⁻, I⁻, and K⁺.

Works cited

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