Supporting Information for

In situ study of competitive adsorption of ions at organic-aqueous two phase interface: The essential role of Hofmeister effect

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Details of molecular dynamic simulations

The aqueous box containing different concentration of ions was constructed in a box with the size of 70×70×70 Å^3.The components in the systems were given in the Table S1 in the supporting information. First, the energies of the initial configuration in simulation boxes were minimized by using the steepest descent algorithm. Afterward, the reasonable size of simulation box was obtained with 1 ns constant-NPT simulation (time step 1 fs). Then, the pre-equilibrium of system was conducted with 0.5 ns constant-NVT simulation (time step 1 fs). Finally, two dichloromethane organic boxes with a thickness of 50 Å were added at the both sides of aqueous box. A constant-NVT simulation was performed for 50 ns to make sure that systems reached the equilibrium. Langevin thermostat was used to control temperature at 298 K.[1] Langevin barostat was used to control pressure at 1 atm.[2] The longrange electrostatic interactions was calculated by using particle mesh ewald (PME) method.[2] Lennard-Jones (LJ) pair potentials were evaluated within a cutoff of 1.2 nm. Lorentz-Berthelot rules was used to calculate the cross-interaction parameters.[3] VMD was used to analyze the trajectory of simulation.[4]

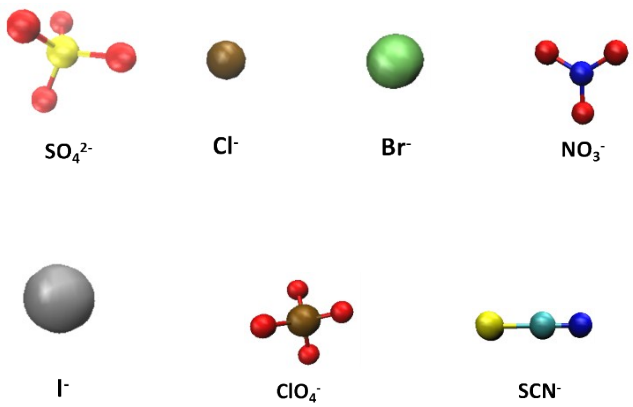
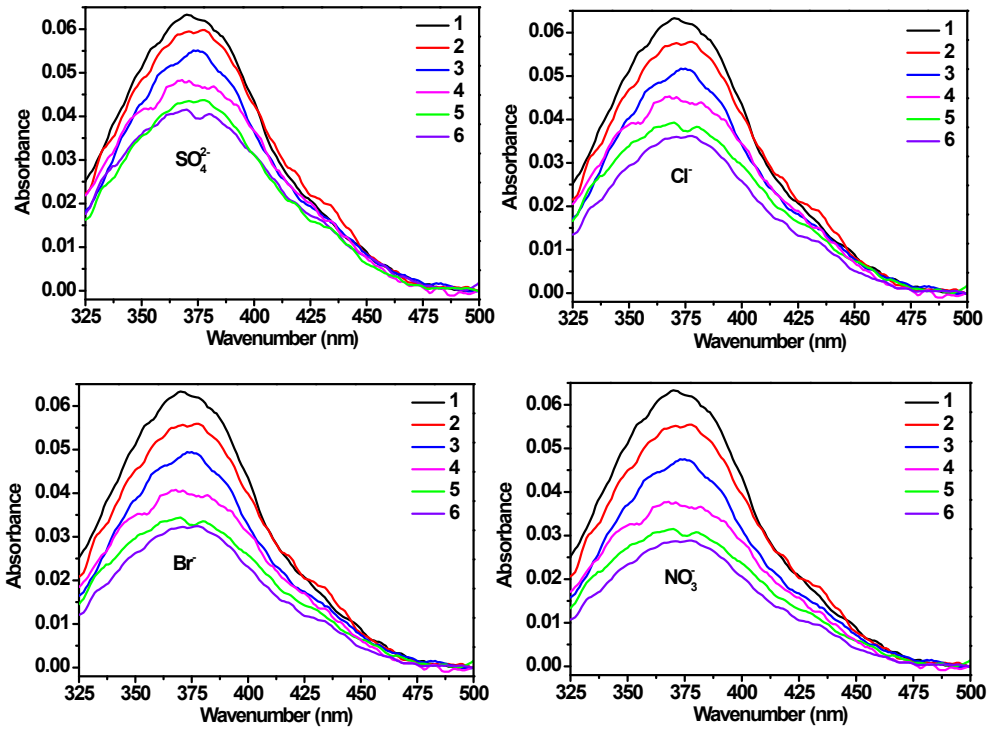


Figure S1. The optimal geometry structure of anions.

Table S1. Number of different components in the systems investigated.

Components	Water	Na^+	CrO_4^{2-}	X[a]	CH_2Cl_2
CrO_4^{2-}-SO_4^{2-}	9999	1300	50	600	4000
CrO_4^{2-}-Cl^-	9999	700	50	600	4000
CrO_4^{2-}-Br^-	9999	700	50	600	4000
CrO_4^{2-}-NO_3^-	9999	700	50	600	4000
CrO_4^{2-}-I^-	9999	700	50	600	4000
CrO_4^{2-}-ClO_4^-	9999	700	50	600	4000
CrO_4^{2-}-SCN^-	9999	700	50	600	4000

a) X represent SO_4^{2-}, Cl^-, Br^-, NO_3^-, I^-, ClO_4^-, SCN^-, in different systems.



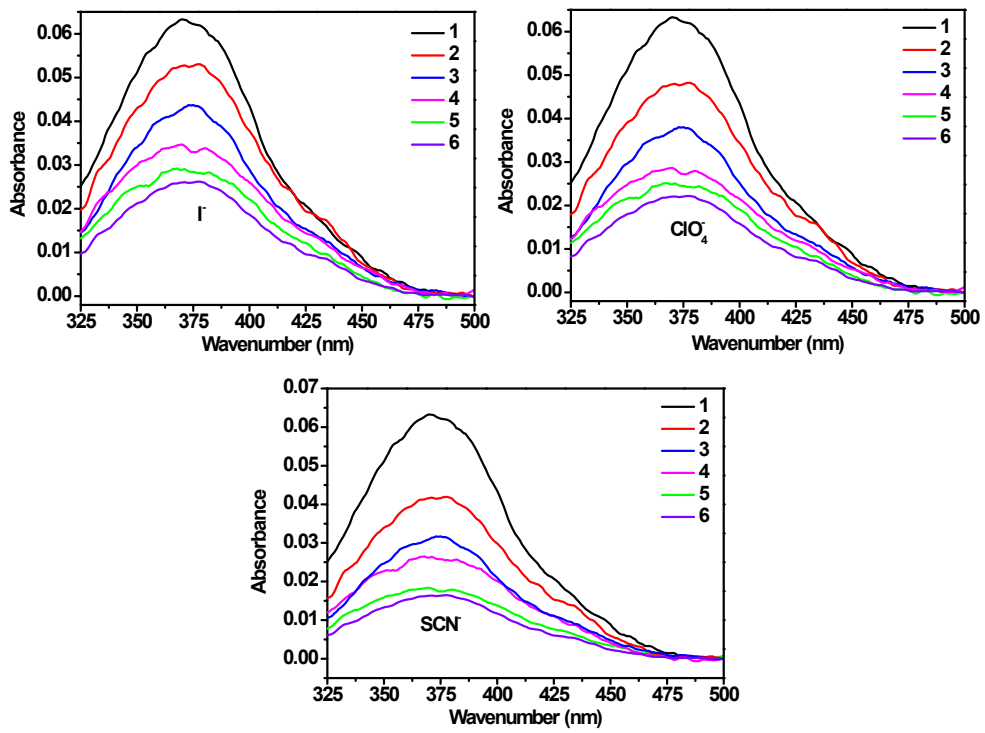


Figure S2. The UV-visible attenuated total reflection spectroscopy of Na_2CrO_4 solutions with different concentration of various salt ions (curves 1, 2, 3, 4, 5, 6 represent different salts (Na_2SO_4, NaCl, NaBr, $NaNO_3$, NaI, $NaClO_4$, NaSCN) concentration of 0, 0.04, 0.1, 0.15, 0.3, 0.5 mol/L, respectively, the concentration of chromate ions in the aqueous solutions were 5 mmol/L, aqueous pH were 12).

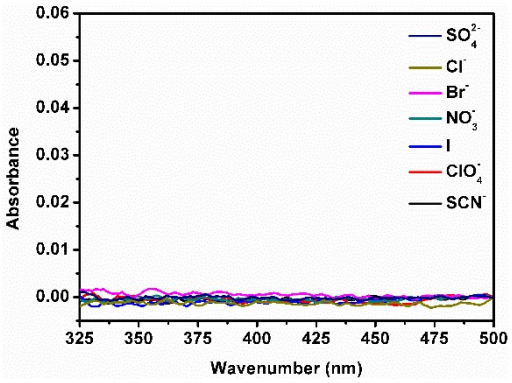


Figure S3. The UV-visible attenuated total reflection spectroscopy of salt solutions with various salt ions and corresponding ATR-UV absorbance for different salt ions. (The concentration of salt ions in the aqueous solutions were 0.5 mol/L, aqueous pH were 12)

References:

[1] S. E. Feller, Y. Zhang, R. W. Pastor, B. R. Brooks, Constant-pressure molecular-dynamic simulation-the langevin-piston method, J. Chem. Phys. 103 (1995) 4613−4621.

[2] T. Darden, D. York, L. Pedersen, Particle mesh ewald-an n.log(n) method for ewald sums in large systems, J. Chem. Phys. 98 (1993) 10089−10092.

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[4] W. Humphrey, A. Dalke, K. Schulten, VMD: visual molecular dynamics J. Mol. Graph. 14 (1996) 33−38.