**Chimie Macromolélaire et Supramoléculaire : COR-709**

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# Tableaux des propriétés des liaisons non-covalents

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**Table 1: Types of electrostatic interactions and their interaction energies.[1, 2]**

| type | interaction energy | comments / distance dependence |
|---|---|---|
| charge-charge | $U = \frac{q_1 q_2}{4\pi\varepsilon\varepsilon_0 r}$ | Coulomb energy<br>long range (~ $r^{-1}$) |
| charge-dipole<br>(fixed dipole) | $U = -\frac{q\mu\cos\theta}{4\pi\varepsilon\varepsilon_0 r^2}$ | long range (~ $r^{-2}$) |
| charge-dipole<br>(free dipole rotation) | $U = -\frac{q^2\mu^2}{6(4\pi\varepsilon\varepsilon_0)^2 kTr^4}$ | medium range (~ $r^{-4}$) |
| dipole-dipole<br>(fixed dipole) | $U = -\frac{\mu_1\mu_2}{4\pi\varepsilon\varepsilon_0 r^3}(2\cos\theta_1\cos\theta_2 - \sin\theta_1\cos\phi\sin\theta_2)$ | medium range (~ $r^{-3}$) |
| dipole-dipole<br>(free dipole rotation) | $U = -\frac{\mu_1^2\mu_2^2}{3(4\pi\varepsilon\varepsilon_0)^2 kTr^6}$ | Keesom energy (Van-der-Waals energy); short range (~ $r^{-6}$) |
| charge-nonpolar | $U = -\frac{q^2\alpha}{2(4\pi\varepsilon\varepsilon_0)^2 r^4}$ | medium range (~ $r^{-4}$) |
| dipole-nonpolar<br>(fixed dipole) | $U = -\frac{\mu^2\alpha(1+3\cos^2\theta)}{2(4\pi\varepsilon\varepsilon_0)^2 r^6}$ | short range (~ $r^{-6}$) |
| dipole-nonpolar<br>(free dipole rotation) | $U = -\frac{\mu^2\alpha}{(4\pi\varepsilon\varepsilon_0)^2 r^6}$ | Debye energy (Van-der-Waals energy); short range (~ $r^{-6}$) |
| nonpolar-nonpolar | $U = -\frac{3}{2}\frac{\alpha_1\alpha_2}{(4\pi\varepsilon\varepsilon_0)^2 r^6}\frac{I_1 I_2}{I_1 + I_2}$ | London dispersion energy (Van-der-Waals energy);<br>short range (~ $r^{-6}$) |

$U$: interaction energy, $q$: charge, $\mu$: dipole, $\alpha$: polarizability, $\varepsilon$: dielectric constant of the medium, $\varepsilon_0$: vacuum permittivity ($\varepsilon_0$ = 8.85 · $10^{-12}$ $C^2$ $N^{-1}$ $m^{-2}$), $r$: distance, $\theta$: angle between dipole vector and vector connecting centers of mass of interacting particles, $\phi$: polar angle of second dipole, $I$: first ionization potential, $k$: Boltzmann constant, $T$: temperature

**Table 2: Association constants $K_a$ and free ion-pair interaction enthalpies $\Delta G$ for tetra(*n*-butyl)ammonium perchlorate in different solvents with dielectric constants $\varepsilon$.[3]**

| solvent | $\varepsilon$ | $K_a$ (l mol$^{-1}$) | $-\Delta G$ (kJ mol$^{-1}$) |
|---|---|---|---|
| dioxane | 2.2 | ca. $10^{19}$ | 109 |
| benzene | 2.3 | $3 \cdot 10^{17}$ | 100 |
| anisole | 4.4 | $10^{9}$ | 52 |
| 1,2-dichloroethane | 10.1 | 6,500 | 22 |
| 1-butanol | 20.4 | 2,200 | 19 |
| acetone | 20.7 | 200 | 13 |
| acetonitrile | 37.5 | 53 | 10 |
| water | 78.4 | - | - |

**Table 3: Gas-Phase Cation-π Interaction Strengths.[4]**

| cation | *molecule* | $\Delta H$ (kJ mol$^{-1}$) |
|---|---|---|
| $Li^+$ | $C_6H_6$ | 160.1 |
| $Na^+$ | $C_6H_6$ | 117.0 |
| $K^+$ | $C_6H_6$ | 79.4 |
| $K^+$(benzene) | $C_6H_6$ | 75.2 |
| $K^+(benzene)_2$ | $C_6H_6$ | 60.2 |
| $K^+(benzene)_3$ | $C_6H_6$ | 52.7 |
| $K^+$ | $H_2O$ | 74.8 |
| $NH_4^+$ | 1,4-$C_6H_4F_2$ | 54.3 [a] |
| $NH_4^+$ | $C_6H_5F$ | 60.2 [a] |
| $NH_4^+$ | $C_6H_6$ | 80.7 |
| $NH_4^+$ | 1,3,5-$C_6H_3(CH_3)_3$ | 91.1 |
| $NH_4^+$ | $C_2H_4$ | 41.8 |
| $CH_3NH_3^+$ | $C_6H_6$ | 78.6 |
| $CH_3NH_3^+$ | cyclohexene | 48.5 |
| $(CH_3)_4N^+$ | $C_6H_6$ | 39.3 |
| $(CH_3)_4N^+$ | $C_6H_5CH_3$ | 39.7 |

[a] geometry unknown, may not be cation-π complex.

**Table 2.4: Properties of hydrogen bonds.[3]**

| | *strong* | *moderate* | *weak* |
|---|---|---|---|
| A-H•••B interaction | mainly covalent | mainly electrostatic | electrostatic |
| bond energy (kJ $mol^{-1}$) | 60 - 160 | 15 - 60 | < 12 |
| bond legths (Å) | | | |
| H•••B | 1.2 - 1.5 | 1.5 -2.2 | 2.2 - 3.2 |
| A•••B | 2.2 - 2.5 | 2.5 -3.2 | 3.2 - 4.0 |
| bond angles ($^o$) | 175 - 180 | 130 - 180 | 90 - 150 |
| $^1$H NMR shifts (Δppm) | 14 - 22 | < 14 | |
| IR vibration shifts (%) | 25 % | 10 - 25 % | < 10 % |

**Table 2.5: Typical bond energies and bond lengths of moderate hydrogen bonds as they often occur in biomolecules.[5]**

| **A-H•••B** | *-ΔG (kJ $mol^{-1}$)* | *bond length (Å)* |
|---|---|---|
| O-H•••O | 22 | 2.70 |
| O-H•••$O^-$ | 15 | 2.63 |
| O-H•••N | 15 – 20 | 2.88 |
| $N^+$-H•••O | 25 – 30 | 2.93 |
| N-H•••O | 15 – 25 | 3.04 |
| N-H•••N | 17 | 3.10 |
| S-H•••S | 7 | |

## References:


[1] J. N. Israelachvili, *Intermolecular and Surface Forces*, Academic Press, London/UK, **1991**.

[2] *Quantitative determination of noncovalent binding interactions using soft ionization mass spectrometry*, J. M. Daniel, S. D. Friess, S. Rajagopalan, S. Wendt, R. Zenobi, *Int. J. Mass Spectrom.* **2002**, *216*, 1-27.

[3] N. Isaacs, *Physical Organic Chemistry*, 2nd ed., Longman, Harlow/UK, **1995**.

[4] *The cation-π interaction*, J. C. Ma, D. A. Dougherty, *Chem. Rev.* **1997**, *97*, 1303-1324.

[5] P. R. Bergethon, *The Physical Basis of Biochemistry: The Foundations of Molecular Biophysics*, Springer, Berlin, **2000**.