Supporting Information

Predictions of Micelle – Water Partition Coefficients and Retention in Micellar Electrokinetic Chromatography from Solute Structure: II. Fragmental Constant Approach (AC0498718)

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Table S1. Correction rules of various intramolecular effects and interactions. k_i values are the multiples of C_m in Eq. 1 [from the work of Rekker for the octanol water system, Ref. 4]

Correction Factor	k_i	**Example**
Saturated aliphatic hydrocarbon chains	+2	n-Butane
Saturated aliphatic hydrocarbon rings	+2	Cyclopentane
Exception	+1	Cylcopropane
Double bonds	0	Ethene
Triple bonds	-1	Ethyne
Extended chain conjugation	+2	1,3-Butadiene
Aromatic hydrocarbons	+1	Benzene
Aromatic condensation	+1	Naphthalene
Aromatic to Aromatic conjugation (Ar-Ar)	+1	Biphenyl
Cross-conjugation	+1	Benzophenone
Proximity effect over 2 C's	+2	Alprenolol
Proximity effect over 1 C	+3	Lidocaine
XCX(3)	+6	Trichloromethane
XCX(4)	+9	Tetrachloromethane
Exception	+12	Tetrafluoromethane
Electronegativity facing alkyl bulk: quaternary C	-2	2-Methylpropan-2-ol
Electronegativity facing alkyl bulk: tertiary C	-1	Propan-2-ol
Oxygen bound to aromatics through 1 C	+1	Benzyl alcohol
Hydrogen bonding	+3	2-Hydroxyacetophenone
Steric hinderance of resonance	-1 to –5	2,6-Dimethyl aniline
Resonance interaction	+2	4-Nitroaniline

Table S2. Fragmental constants for the aromatic and aliphatic fragments; n is the number of solutes, s is the standard error of the regression, and F is the F-statistic which is a reflection of the goodness of a fit.

Fragment	Regression I	Regression II
C_6H_5	1.820 (0.030)	N/a
C_6H_4	1.680 (0.059)	N/a
C_6H_3	1.552 (0.092)	N/a
CH_3	0.578 (0.028)	0.620 (0.003)
CH_2	0.390 (0.089)	0.423 (0.000)
CH	0.238 (0.040)	0.223 (0.005)
O	-0.251 (0.018)	-0.693 (0.008)
C(O)	-0.263 (0.018)	-0.660 (0.007)
CHO	0.090 (0.032)	-0.335 (0.006)
CN	0.092 (0.030)	-0.304 (0.007)
NO_2	0.142 (0.030)	-0.153 (0.007)
OH	-0.183 (0.031)	-0.627 (0.006)
NH_2	-0.190 (0.031)	-0.649 (0.006)
NH	-0.330 (0.034)	-0.969 (0.009)
C(O)O	0.038 (0.018)	-0.365 (0.006)
OC(O)	-0.261 (0.027)	-0.390 (0.008)
$C(O)NH_2$	-0.229 (0.049)	-0.756 (0.009)
F	0.192 (0.029)	-0.081 (0.010)
Cl	0.657 (0.029)	0.302 (0.004)
Br	0.801 (0.030)	0.498 (0.005)
I	1.033 (0.031)	0.816 (0.007)
CF_3	0.779 (0.030)	N/a
n	205	151
R^2	0.995	0.999
s	0.070	0.017
F	1674	62,517

The values in parentheses are the standard deviations of each fragment

Aromatic f_i – fragments determined with observed log K_{mw}

Aliphatic f_i – fragments determined with predicted log K_{mw} (LSER)

Table S3. Fragmental constants using a combination of aromatic and aliphatic solutes in the regression of Eq. 4. The values in parentheses are the standard deviations of each fragment

Fragment	Regression III	Regression IV
C	0.192 (0.004)	0.201 (0.004)
H	0.120 (0.002)	0.110 (0.002)
Ar-O	-0.226 (0.015)	-0.232 (0.013)
Ar-C(O)	-0.250 (0.015)	-0.257 (0.013)
Ar-CHO	0.111 (0.017)	0.083 (0.016)
Ar-CN	0.111 (0.014)	0.084 (0.013)
Ar-NO_2	0.160 (0.014)	0.134 (0.013)
Ar-OH	-0.268 (0.020)	-0.288 (0.019)
Ar-NH_2	-0.144 (0.015)	-0.171 (0.014)
Ar-NH	-0.395 (0.032)	-0.404 (0.029)
Ar-C(O)O	0.057 (0.015)	0.049 (0.014)
Ar-OC(O)	-0.238 (0.022)	-0.248 (0.020)
Ar-C(O)NH_2	-0.212 (0.036)	-0.243 (0.033)
Ar-F	0.207 (0.013)	0.180 (0.012)
Ar-Cl	0.662 (0.013)	0.637 (0.012)
Ar-Br	0.807 (0.014)	0.780 (0.013)
Ar-I	1.037 (0.015)	1.010 (0.014)
Ar-CF_3	0.798 (0.013)	0.772 (0.012)
al-O	-0.641 (0.028)	-0.520 (0.029)
al-C(O)	-0.618 (0.022)	-0.486 (0.025)
al-CHO	-0.358 (0.023)	-0.250 (0.024)
al-CN	-0.316 (0.026)	-0.222 (0.026)
al-NO_2	-0.168 (0.024)	-0.070 (0.025)
al-OH	-0.675 (0.018)	-0.538 (0.023)
al-NH_2	-0.676 (0.021)	-0.563 (0.024)
al-NH	-0.919 (0.031)	-0.796 (0.032)
al-C(O)O	-0.319 (0.019)	-0.192 (0.023)
al-OC(O)	-0.336 (0.026)	-0.218 (0.030)
al-C(O)NH_2	-0.761 (0.031)	-0.674 (0.030)
al-F	-0.095 (0.035)	0.002 (0.034)
al-Cl	0.271 (0.015)	0.352 (0.016)
al-Br	0.469 (0.019)	0.580 (0.022)
al-I	0.815 (0.024)	0.917 (0.025)
C_m		0.090 (0.010)
Coefficient	0.065	0.009
n	344	344
R^2	0.997	0.998
s	0.060	0.054
F	3,551	4,195