Adsorption of Organic Micropollutants to Biosolids-Derived Biochar: Estimation of Thermodynamic Parameters

Supplemental Information

Yiran Tong[a,α], Brooke K. Mayer[a] Patrick J. McNamara[a] *

[a] Department of Civil, Construction and Environmental Engineering, Marquette University, 1637 W. Wisconsin Ave., Milwaukee, WI 53233, USA

*Corresponding author
Email:Patrick.McNamara@marquette.edu
Phone: 414-288-2188

[α]Current affiliation: Department of Civil, Environmental and Geo- Engineering, University of MN-Twin Cities

The supplemental information consists of 9 sections (including 4 figures and 7 tables) describing:
S1: LC-MS operation and analysis
S2: Isotherm fitting parameters for micropollutants under single-solute conditions
S3: Isostere curves for micropollutants under single-solute conditions
S4: Calculations of exchange or adsorption capacity and recovery rate
S5: Single-solute van't Hoff curves for calculating change of enthalpy, free energy and entropy
S6: Comparison of significant difference between single-solute and multi solute isotherms
S7: Isostere curves for micropollutants under multi-solute conditions
S8: Multi-solute van't Hoff curves for calculating change of enthalpy, free energy and entropy
S9: Comparison of differences between single-solute and multi-solute adsorption enthalpy and entropy changes

S1: LC-MS operation and analysis

Internal standards of benzyldimethyldodecylammonium chloride (BAC-C12), licarbazepine (L-CBZ), estrone (E1), and 13C-TCS methanol stock solutions were added in 2 mL LC-MS vials, separately for single-solute experiments and all together for multi-solute experiments. The solvent was evaporated before samples were added. The target concentration of the internal standards was 100 µg/L. Filtered water samples were mixed with methanol (50:50) to make 1 mL solutions in the vials.

For BAC-C10 and TCS, a binary gradient of Milli-Q water (Pump A) and 100% HPLC-grade methanol (Pump B) was used as the eluent. An isocratic flow of 0.4 mL/min (4% Pump A+96% Pump B) was maintained for 10 min. Sample injection was 5 µL.

For CBZ, a binary gradient of Milli-Q water (Pump A) and HPLC-grade acetonitrile in combination of 0.1% formic acid (v/v) (Pump B) was the eluent. Pump B started at 20% and ramped up to 95% at 9 min. The gradient maintained for 1 min and decreased to 20% at the 12th min. The binary eluent flow rate was 0.3 mL/min. Sample injection volume was 10 µL.

For E2 and EE2, the eluents were Milli-Q water (Pump A) and 100% HPLC-grade methanol (Pump B). Pump B started at 65% and ramped up to 85% at the 8th min. The gradient maintained for 5 min and decreased to 35% at the 15th min. The binary eluent flow rate was 0.4 mL/min. Sample injection volume was 15 µL.

All samples were passed through a Phenomenex® (Torrance, CA) Luna 3u C18 reverse-phase column.

The MS detection limits of BAC-C10, CBZ, E2, EE2, TCS and their internal standards are listed in Table 5A. Recovery of tested compounds was 70 – 130%.

Table S1. Mass spectrometry operation parameters for micropollutants and internal standards. For all analyses, the acquisition mode was used for ion monitoring (SIM) and the ionization method was electrospray ionization (ESI).

Compound	m/z	Retention time	Internal standard	m/z	Method detection limit (µg/L)
BAC-C10	276	1.4	BAC-C12	304	5
CBZ	237	7.5	L-CBZ	255	4
E2	271	4.2	E1	269	6
EE2	295	4.3			12
TCS	287	2.9	13C-TCS	299	8

S2. Isotherm fitting parameters for micropollutants under single-solute conditions

Adsorption equilibrium data was fit with linear, Langmuir and Freundlich isotherms, due to the isotherms' application for low-concentration (< mg/L) adsorption. As Table S2 shows, K, K_L, and K_f values are partitioning coefficients for linear, Langmuir and Freunlich isotherms, respectively. The portioning coefficients are important because of their relationship with thermodynamic equilibrium coefficients.

Table S2. Isotherm parameters for micropollutants under single-solute conditions

Compound	**Isotherm**	**Parameter**	**4˚C**	**25˚C**	**35˚C**	**50˚C**
BAC-C10	Linear	K	0.469	0.359	0.569	1.03
		B	72.6	472	503	240
		R^2	0.923	0.978	0.711	0.972
CBZ	Linear	K	0.59	0.822	0.715	1.05
		B	155	121	294	269
		R^2	0.908	0.929	0.925	0.999
E2	Freundlich	K_f	23.4	41.0	63.8	106
		n	0.55	0.57	0.51	0.46
		R^2	0.856	0.949	0.954	0.965
	Langmuir	Q_m	1890	9800	3860	7140
		K_L	0.0022	0.0005	0.0058	0.0033
		R^2	0.856	0.900	0.932	0.936
EE2	Linear	K	2.10	4.00	3.80	4.37
		B	244	-31.7	725	837
		R^2	0.987	0.992	0.997	0.966
TCS	Freundlich	K_f	19.4	27.0	207	108
		n	0.73	0.71	0.43	0.58
		R^2	0.974	0.866	0.985	0.959
	Langmuir	Q_m	5440	26800	3650	8340
		K_L	0.0009	0.0002	0.0102	0.0018
		R^2	0.955	0.856	0.945	0.840

S3. Isostere curves for micropollutants under single-solute conditions

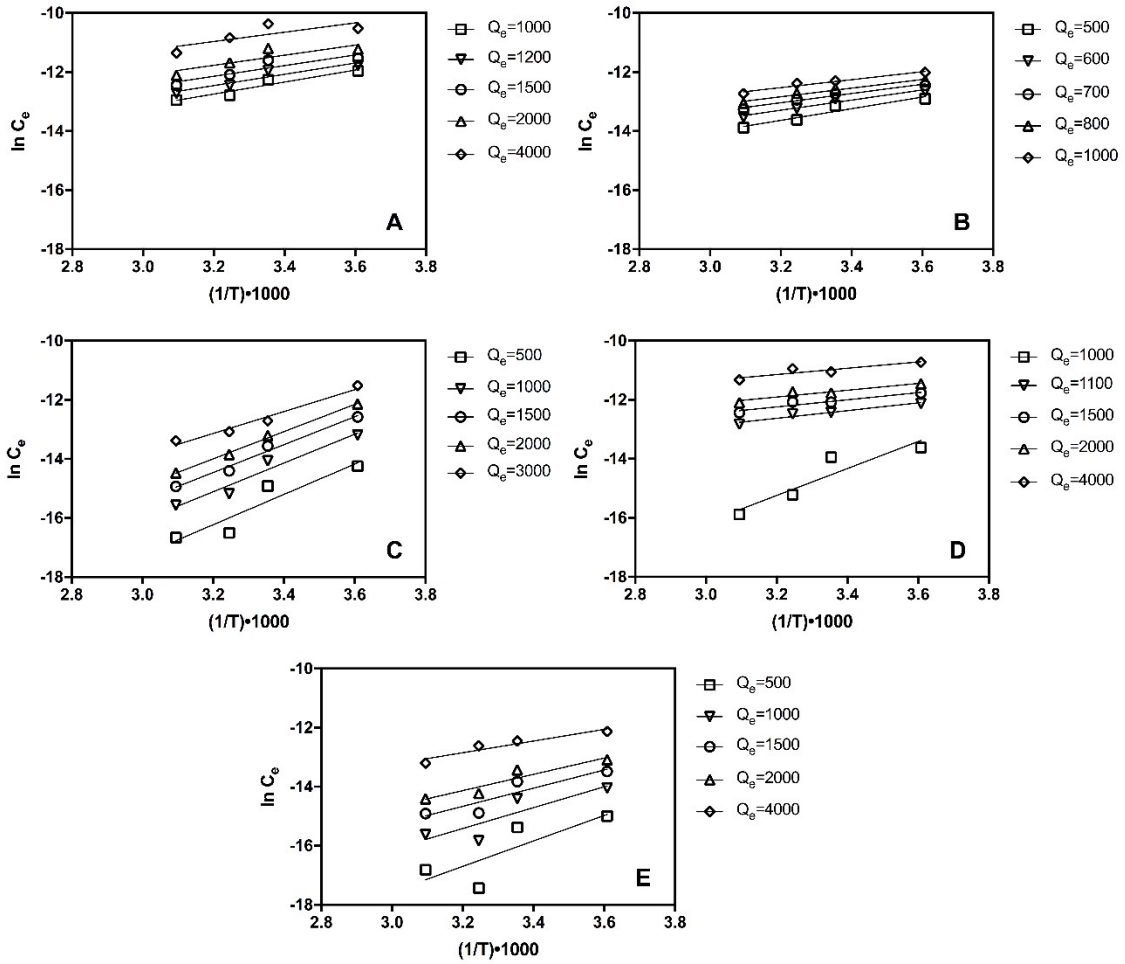

Figure S1. Isostere curves for A) BAC-C10, B) CBZ, C) E2, D) EE2, and E) TCS at multiple surface loading (Q_e) values, in single-solute tests.

Table S3. Slopes of isostere curves for micropollutants under single-solute conditions

Compound	Q_e mmol/g biochar	$\ln C_e/(1/T)$
BAC-C10	0.0032	2.03
	0.0038	1.91
	0.0052	1.91
	0.0064	1.81
	0.0128	1.58
CBZ	0.0021	1.97
	0.0025	1.71
	0.0030	1.56
	0.0034	1.47
	0.0042	1.35
E2	0.0018	5.13
	0.0037	4.86
	0.0055	4.72
	0.0073	4.61
	0.0110	3.71
EE2	0.0034	6.25
	0.0037	1.85
	0.0052	1.72
	0.0111	1.65
	0.0148	1.54
TCS	0.0017	4.31
	0.0035	3.53
	0.0052	3.08
	0.0069	2.76
	0.0138	1.98

S4. Single-solute van't Hoff curves for calculating change of enthalpy, free energy and entropy

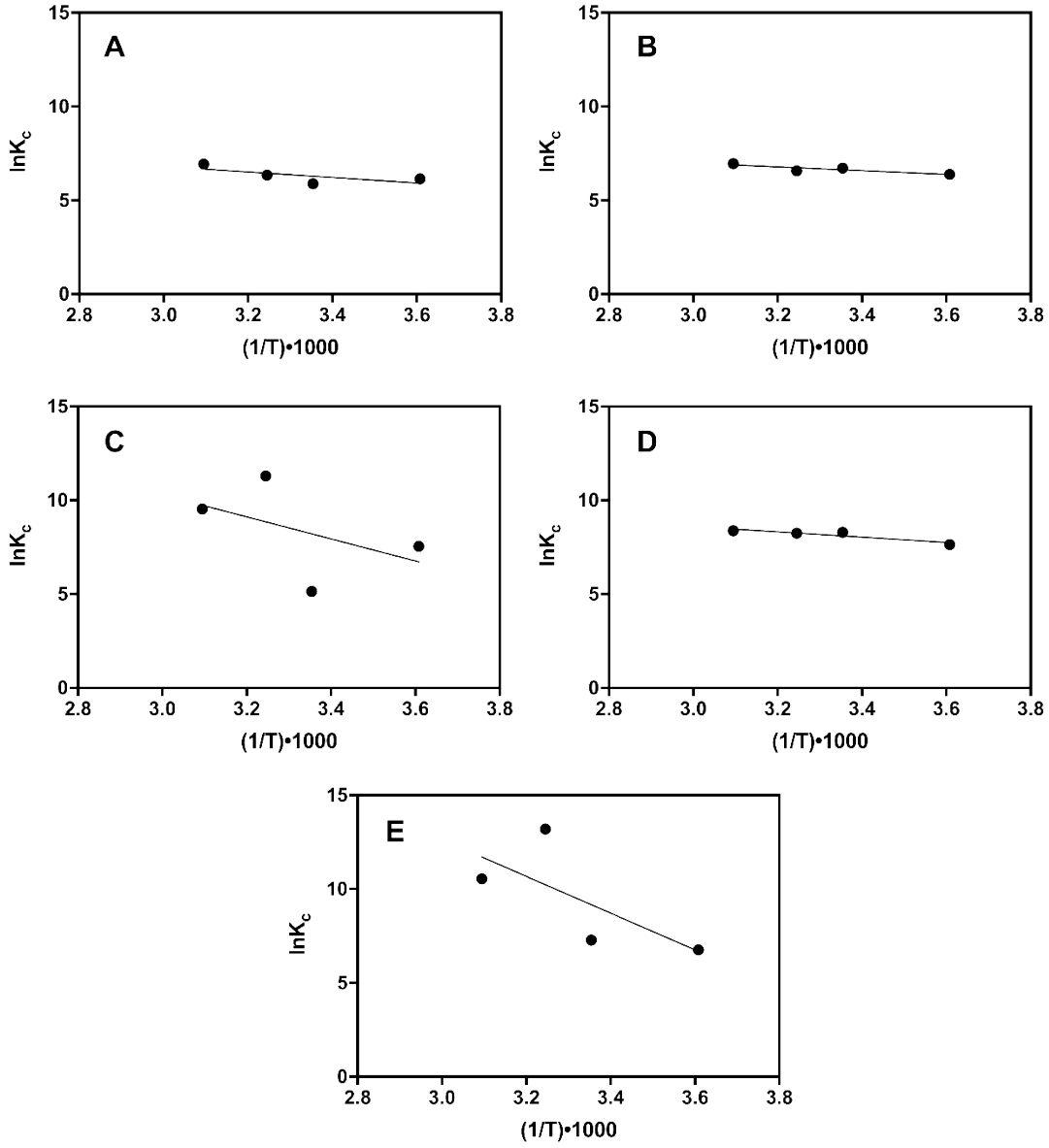

Figure S2. Single-solute van't Hoff curves for A) BAC-C10, B) CBZ, C) E2, D) EE2, and E) TCS.

S5. Isotherm parameters for micropollutants under multi-solute conditions

Table S4. Isotherm parameters for micropollutants under multi-solute conditions

Compound	Isotherm	Parameter	4˚C	25˚C	35˚C	50˚C
BAC-C10	Linear	K	0.63	0.70	0.91	0.47
		B	-118	-17.3	87.8	232
		R^2	0.655	0.672	0.948	0.9999
CBZ	Linear	K	0.57	0.24	0.37	0.81
		B	54.5	252	281	159
		R^2	0.850	0.960	0.981	0.724
E2	Freundlich	K_f	16.7	12.9	109	87.2
		n	0.66	0.81	0.52	0.63
		R^2	0.711	0.977	0.971	0.901
	Langmuir	K_L	1520	2870	2350	3090
		B	494	441	211	228
		R^2	0.663	0.961	0.939	0.924
EE2	Linear	K	0.64	1.48	1.23	1.61
		B	212	308	501	518
		R^2	0.905	0.996	0.842	0.885
TCS	Freundlich	K_f	13.6	54.2	95.9	109
		n	0.75	0.60	0.55	0.51
		R^2	0.812	0.969	0.951	0.910
	Langmuir	K_L	5960	3600	3360	2890
		B	1560	345	130	123
		R^2	0.767	0.954	0.921	0.815

S6. Comparison of significant difference between single-solute and multi-solute isotherms

Table S5. p-values for comparing the difference between single-solute and multi-solute isotherms

Compound	4˚C	25˚C	35˚C	50˚C
BAC-C10	N/A	N/A	0.208	0.062
CBZ	0.926	0.012	0.254	0.589
E2	0.017	<0.0001	<0.0001	<0.0001
EE2	0.0003	<0.0001	0.0002	0.003
TCS	0.035	0.850	0.072	<0.0001

N/A indicates that linear fitting of BAC-C10 in multi-solute condition was poor (<0.7); therefore, they cannot be compared with single-solute conditions.

S7. Isostere curves for micropollutants under multi-solute conditions

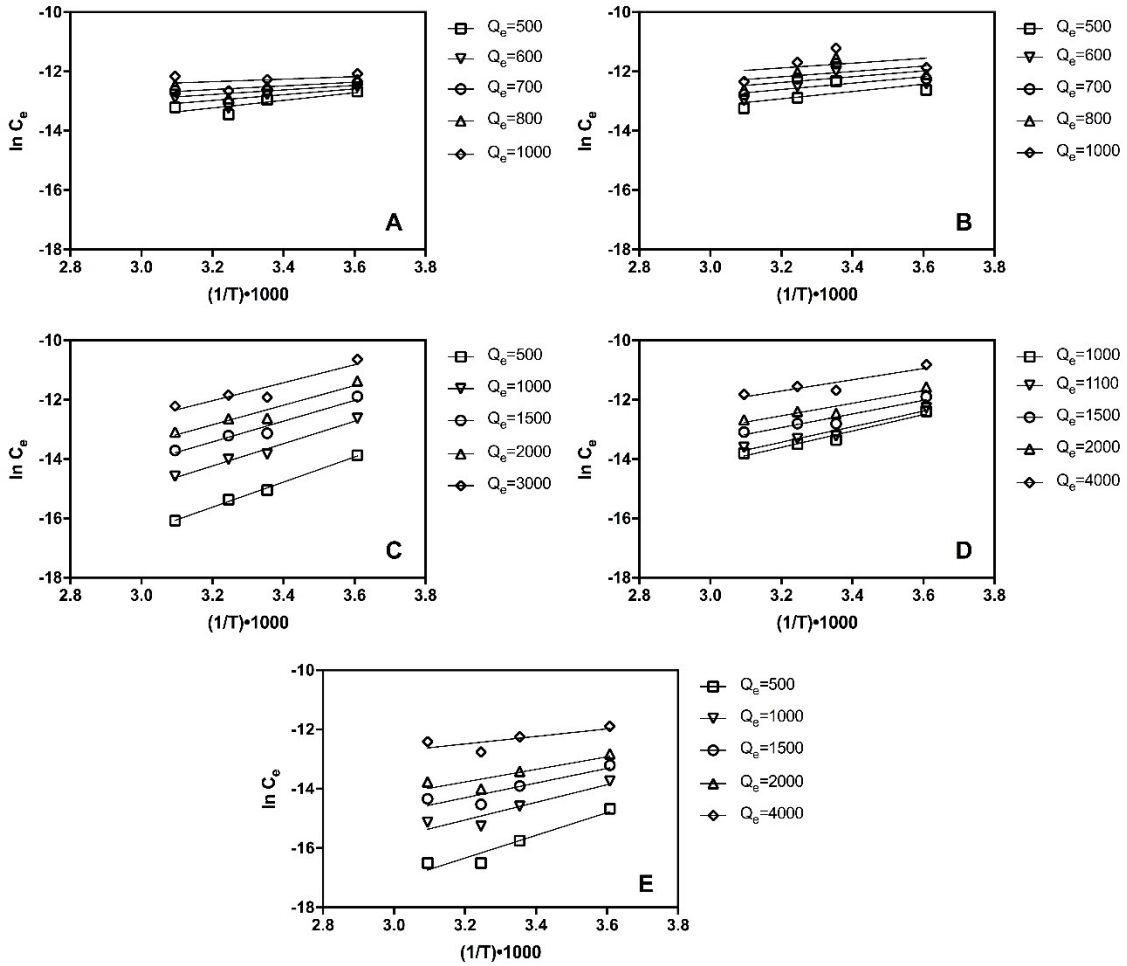

Figure S3. Isostere curves for A) BAC-C10, B) CBZ, C) E2, D) EE2, and E) TCS at multiple surface loading (Q_e) values in multi-solute tests.

Table S6. Slopes of isostere curves for micropollutants under multi-solute conditions

Compound	Q_e mmol/g biochar	$\ln C_e/(1/T)$
BAC-C10	0.0016	1.28
	0.0019	0.97
	0.0024	0.77
	0.0026	0.62
	0.0032	0.42
CBA	0.0021	1.23
	0.0025	1.07
	0.0030	0.97
	0.0034	0.90
	0.0042	0.81
E2	0.0018	4.23
	0.0037	3.76
	0.0055	3.49
	0.0074	3.30
	0.0110	3.03
EE2	0.0034	2.76
	0.0037	2.62
	0.0052	2.29
	0.0111	2.12
	0.0148	1.90
TCS	0.0017	3.83
	0.0035	2.97
	0.0052	2.47
	0.0069	2.12
	0.0138	1.27

S8. Multi-solute van't Hoff curves for calculating change of enthalpy, free energy and entropy

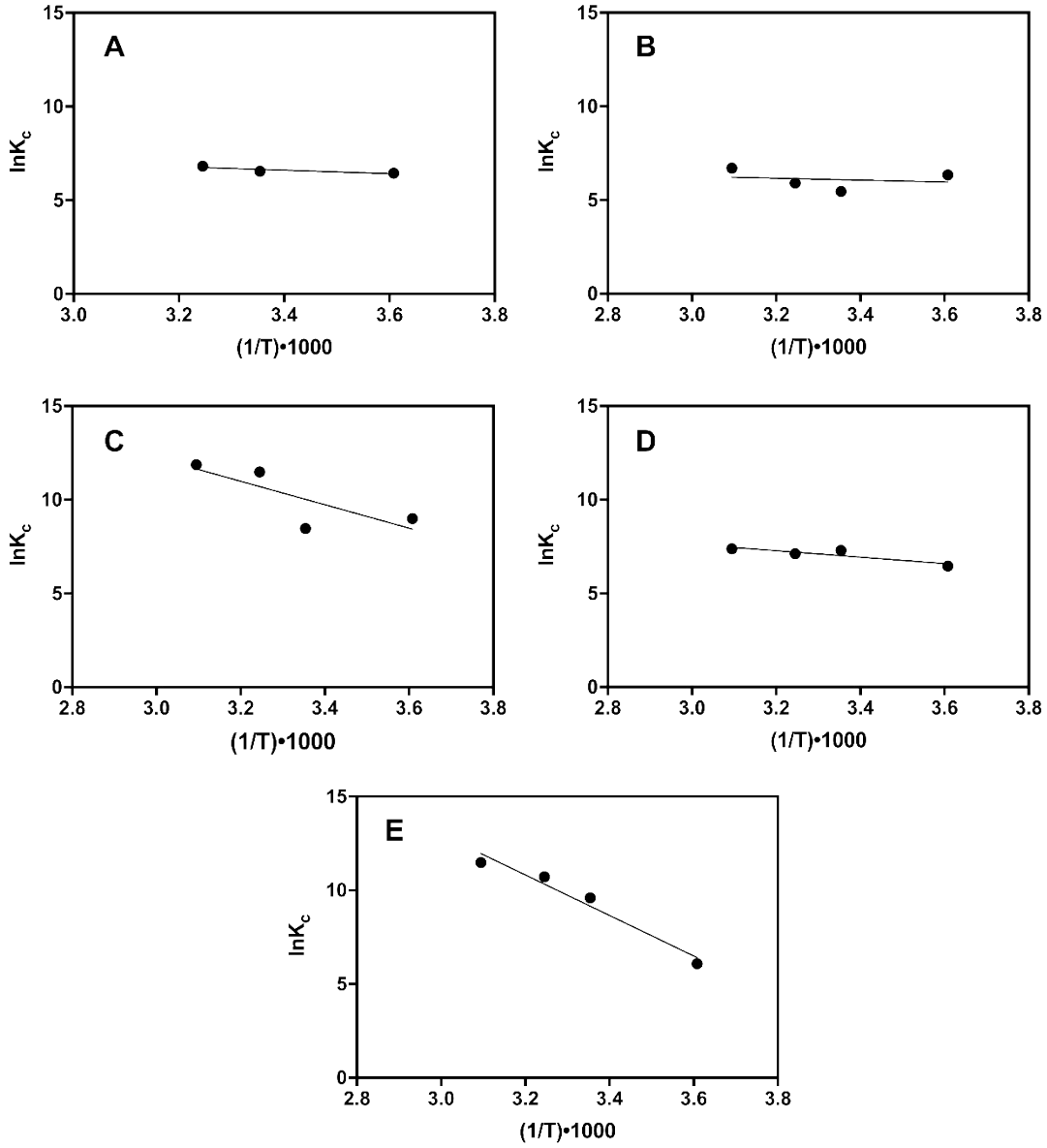

Figure S4. Multi-solute van't Hoff curves for A) BAC-C10, B) CBZ, C) E2, D) EE2, and E) TCS.

S9. Comparison of differences between single-solute and multi-solute adsorption enthalpy and entropy changes

Table S7. p-values for comparing the difference between single-solute and multi-solute enthalpy and entropy changes

Compound	p for comparing ΔH^0	p for comparing ΔS^0
BAC-C10	0.744	0.166
CBZ	0.795	0.124
E2	0.966	0.248
EE2	0.706	0.0004
TCS	0.894	0.897