

## Supporting Information

# **Solvent and Flow Rate Effects on the Observed Compositional Profiles and the Relative Intensities of Radical and Protonated Species in Atmospheric Pressure Photoionization Mass Spectrometry**

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## Table of Contents

**Table S1.** Properties of solvents used, with cosolvents used in the first and second stages of the study ordered by polarity index

**Table S2.** Design of Experiment Parameters. 3 factors (sample concentration, toluene fraction, and flow rate) were studied using a full factorial  $2^3$  design, using a single replicate of 13 runs including 5 centrepoints. All terms were free from aliasing

**Table S3.** Composer 1.5.7 parameters for the assignment of molecular formulae

**Figure S1.** Summed relative intensity of protonated and radical ion classes assigned in solvent systems initially studied

**Figure S2.** Summed relative intensity of protonated and radical ion classes containing at least one sulfur atom assigned in solvent systems initially studied

**Figure S3.** Hypothetical scheme illustrating ethyl acetate generating sources of labile protons; its resonance stabilized protonated form, and its hydrolysis product acetic acid.  $[H]^+$  may be generated in the source as indicated in Equation scheme 1

**Figure S4.** DBE vs. carbon number plots for N and N[H] classes in toluene:propan-2-ol and toluene:ethyl acetate solvent systems, with squares surrounding corresponding DBE and carbon number values demonstrating the similarity between the species apparent in the N class and N[H] class of each, respectively. The N[H] class was observed at low relative intensity in the toluene:propan-2-ol solvent system, while the N class was not detected in the toluene:ethyl acetate solvent system

**Figure S5.** DBE vs. carbon number plots for S and S[H] classes in toluene:propan-2-ol and toluene:ethyl acetate solvent systems, demonstrating similarity between the species apparent in the S class and S[H] class of each, respectively. The S[H] class and S class were observed at low relative intensity in the toluene:propan-2-ol and toluene:ethyl acetate solvent systems respectively

**Figure S6.** Summed N and N[H] class DBE distribution for the toluene:propan-2-ol solvent system compared the N[H] class DBE distribution for the toluene:ethyl acetate solvent system

**Figure S7.** Summed S and S[H] class DBE distribution for the toluene:propan-2-ol solvent system compared the S[H] class DBE distribution for the toluene:ethyl acetate solvent system

**Figure S8.** DBE distribution of the N[H] class compared between the toluene:ethyl acetate and toluene:propan-2-ol solvent systems

**Figure S9.** Normalized relative intensities of S and S[H] classes for all solvent systems studied

**Figure S10.** Change in S/S[H] with total vapour pressure of solvent system

**Figure S11.** Change in S/S[H] with polarity index of solvent added at 20 v/v % to solvent system

**Figure S12.** Change in  $S/S[H]$  with ionization energy of solvent added at 20 v/v % to solvent system

**Table S4.** Molecular entities with proton affinities between 157.8 and 628 kJmol<sup>-1</sup>. Due to the hazards associated with these, or their lack of stability and commercial availability, in liquid form, they are unsuitable to be used as cosolvents used in this study.

**Figure S13.** Summary of DoE study where response factor is the mean ratio of radical to protonated species (R/P). While higher sample concentration and larger toluene solvent fraction increase radical ion formation, a high flow rate decreases the relative proportion of radical species detected. Red squares are indicative of the effect at the centerpoint of the DoE.

**Figure S14.** Pareto chart of standardized effects for DoE experiments. The response is the mean ratio of radical and protonated species detected (R/P). Factors that exceed the dashed reference line are statistically significant at the  $\alpha = 0.05$  level.

**Figure S15.** Percent change in monoisotopic absolute intensity of model compound spiked into Iraqi crude oil dissolved in different solvent systems with flow rate relative to observed intensity at 1000  $\mu\text{L h}^{-1}$ .

**Table S1.** Properties of solvents used, with cosolvents used in the first and second stages of the study ordered by polarity index

Solvent	Polarity Index	pKa	Ionization Energy / eV	Vapor Pressure / $\text{kJ mol}^{-1}$	Boiling Point / K	Proton Affinity / $\text{kJ mol}^{-1}$
Toluene	2.3	41	$8.828 \pm 0.001$	$37 \pm 3$	$383.8 \pm 0.2$	784.0
n-hexane	0.0	N/A	$10.13 \pm 0.10$	$31 \pm 1$	$341.9 \pm 0.3$	672.5
DCM	3.4	N/A	$11.33 \pm 0.04$	$29.03 \pm 0.08$	$313 \pm 1$	628.0
Propan-2-ol	4.3	17.1	$10.17 \pm 0.02$	$45 \pm 3$	$355.5 \pm 0.4$	793.0
Ethyl acetate	4.3	25	$10.01 \pm 0.05$	$35 \pm 2$	$350.2 \pm 0.2$	835.7
Chloroform	4.4	15.5	$11.37 \pm 0.02$	$31.32 \pm 0.08$	$334.3 \pm 0.2$	157.8 <sup>†</sup>
Acetonitrile	6.2	25	$12.20 \pm 0.01$	$33.45 \pm 0.21$	$354.8 \pm 0.4$	779.2
Acetone	5.1	19.6	$9.703 \pm 0.006$	31.27	$329.3 \pm 0.3$	812
Ethanol	5.2	16	$10.48 \pm 0.07$	$42.3 \pm 0.4$	$351.5 \pm 0.2$	776.4
Acetic Acid	6.2	4.75	$10.65 \pm 0.02$	$51.6 \pm 1.5$	$391.2 \pm 0.6$	783.7

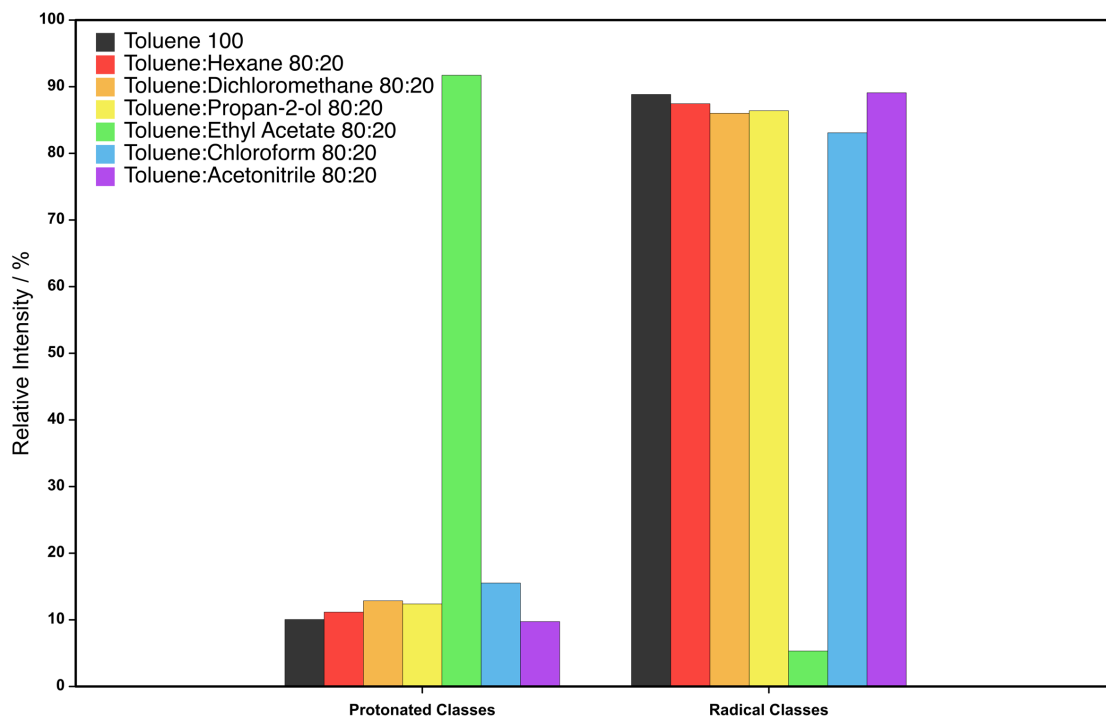
<sup>†</sup>Calculated value.

**Table S2.** Design of Experiment Parameters. 3 factors (sample concentration, toluene fraction, and flow rate) were studied using a full factorial  $2^3$  design, using a single replicate of 13 runs including 5 centrepoints. All terms were free from aliasing

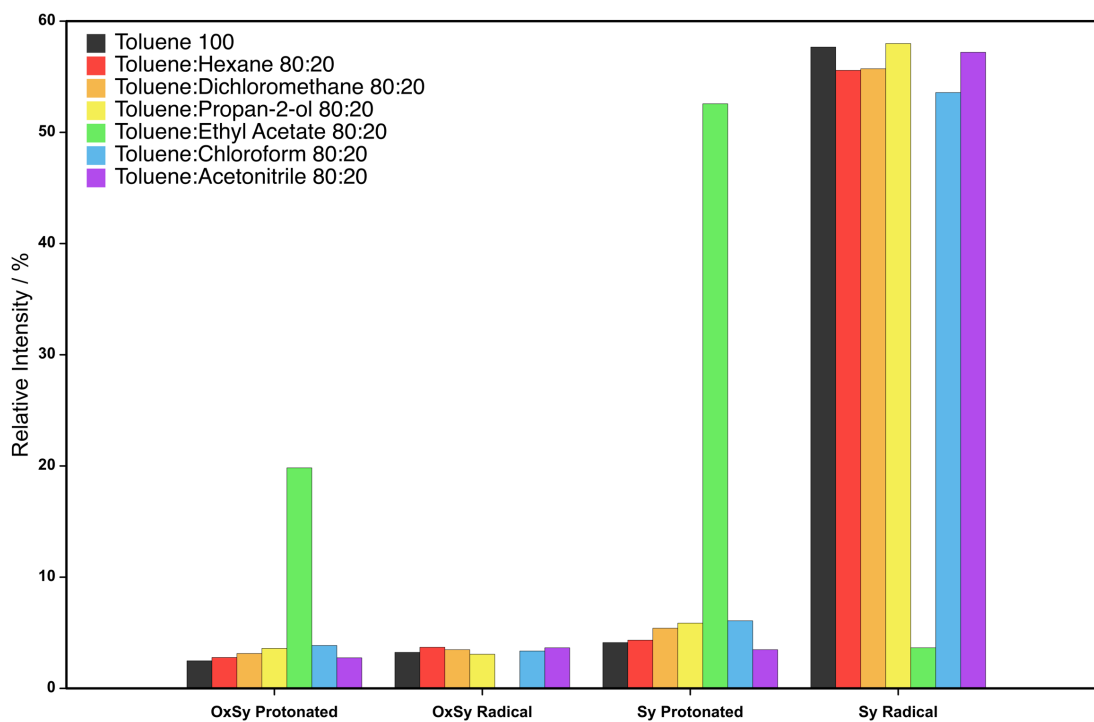
Standard Order	Run Order	Centrepoint?	Blocks	Concentration / mg mL <sup>-1</sup>	Toluene Fraction / %	Flow Rate / μL h <sup>-1</sup>
2	1	No	1	0.300	20	600
4	2	No	1	0.300	100	600
10	3	Yes	1	0.175	60	2300
6	4	No	1	0.300	20	4000
3	5	No	1	0.050	100	600
11	6	Yes	1	0.175	60	2300
9	7	Yes	1	0.175	60	2300
8	8	No	1	0.300	100	4000
13	9	Yes	1	0.175	60	2300
7	10	No	1	0.050	100	4000
12	11	Yes	1	0.175	60	2300
1	12	No	1	0.050	20	600
5	13	No	1	0.050	20	4000

**Table S3.** Composer 1.5.7 parameters for the assignment of molecular formulae

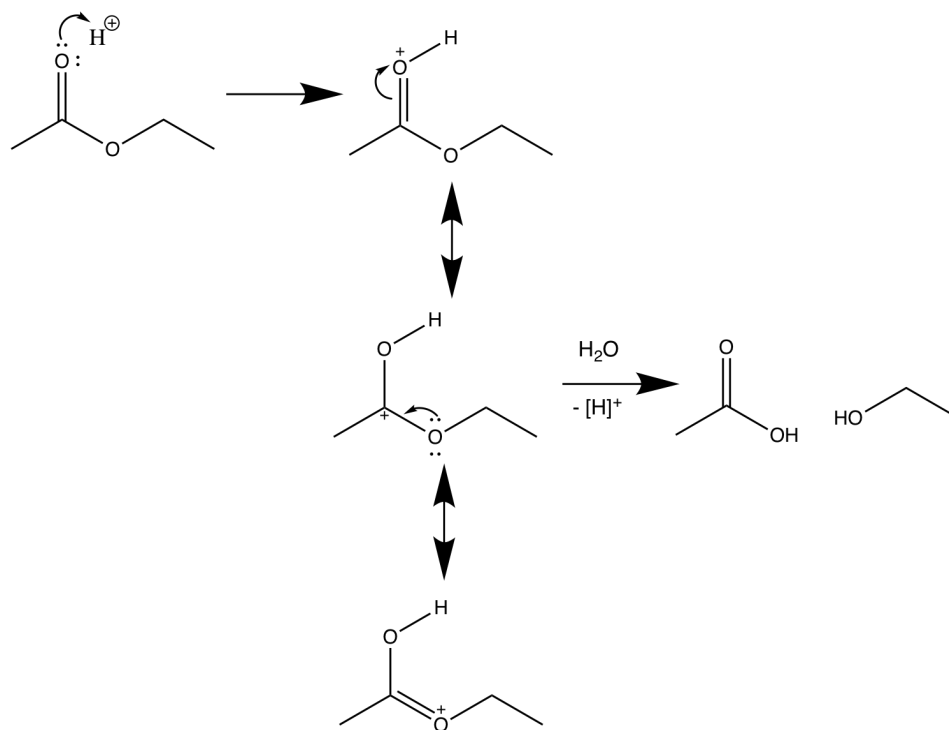
Parameter	Constraints
Polarity	Positive
Ion properties	Adducts = H; allow radical and adduct/loss ions; remove isolated assignments
m/z range	m/z 200-1300
DBE range	-0.5 - 40
Element ranges	C = 0-200; H = 0-1000 ; N= 0-4; O = 0-4; S = 0-6



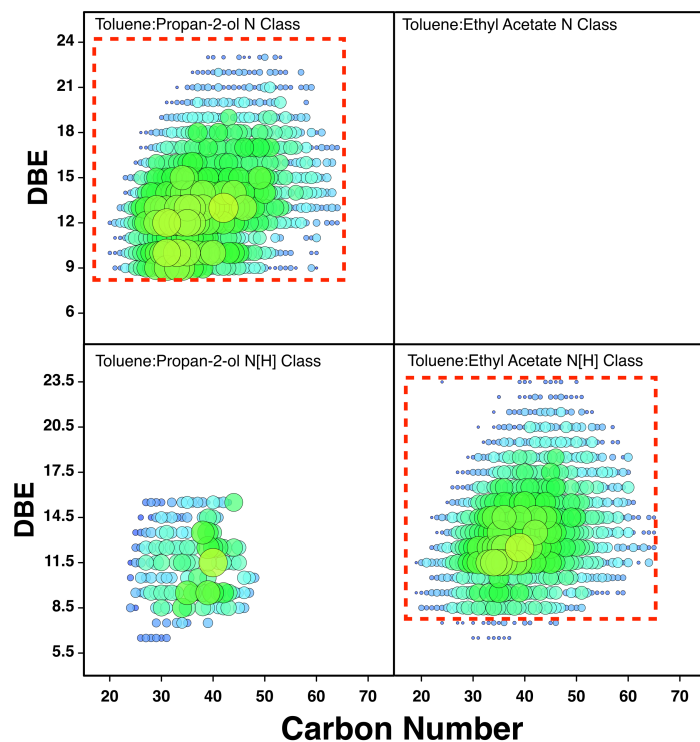
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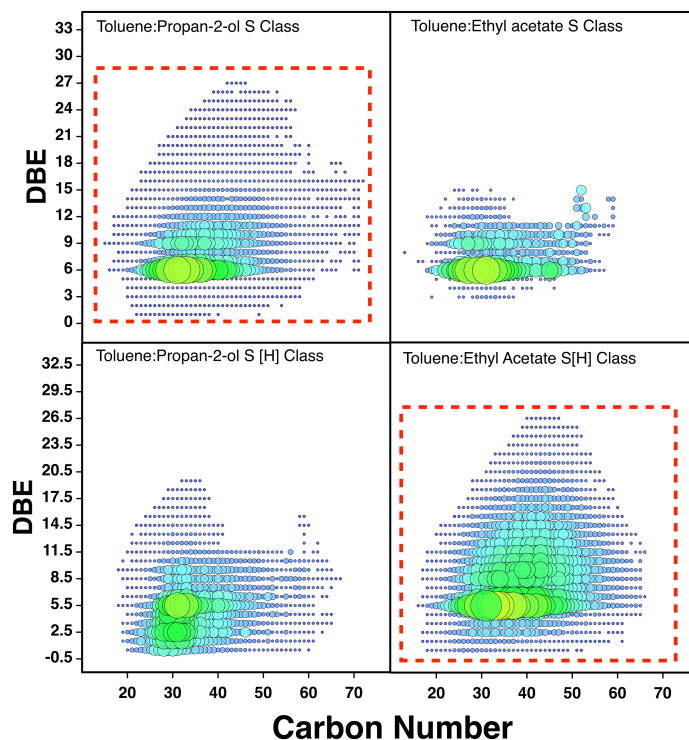


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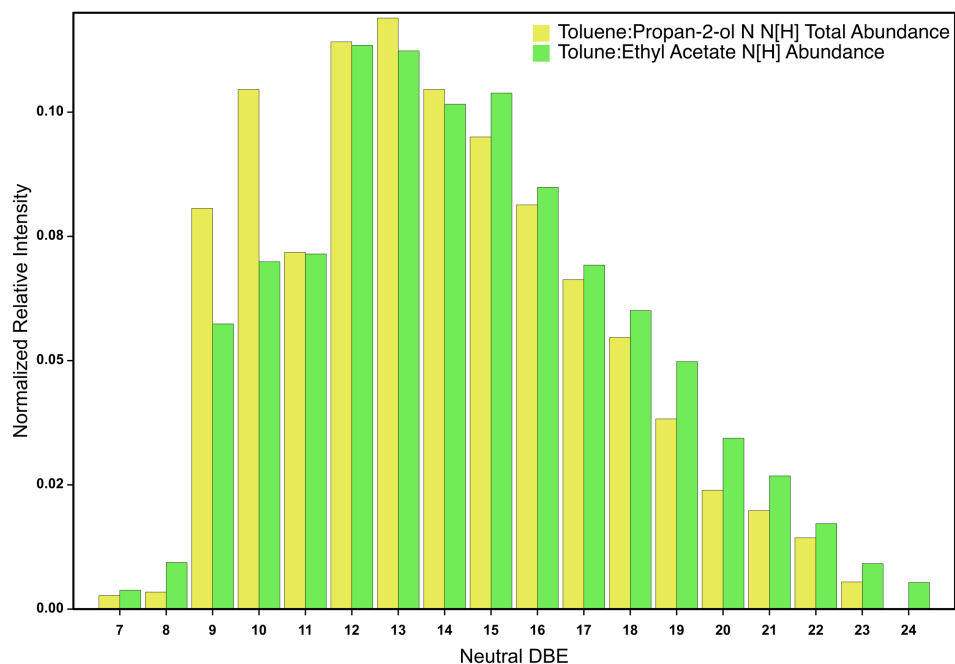


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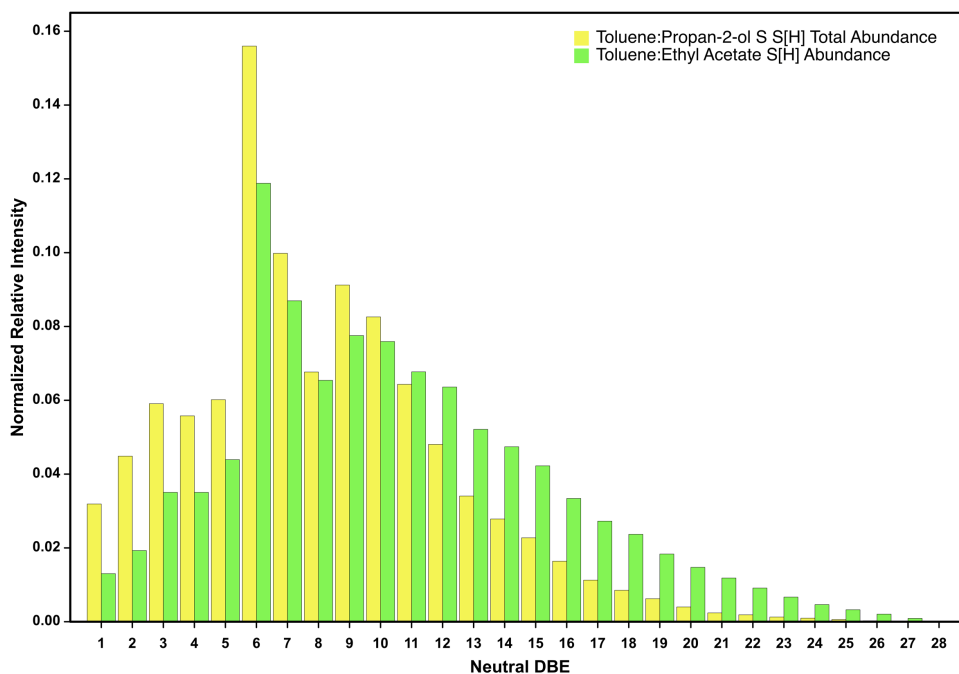




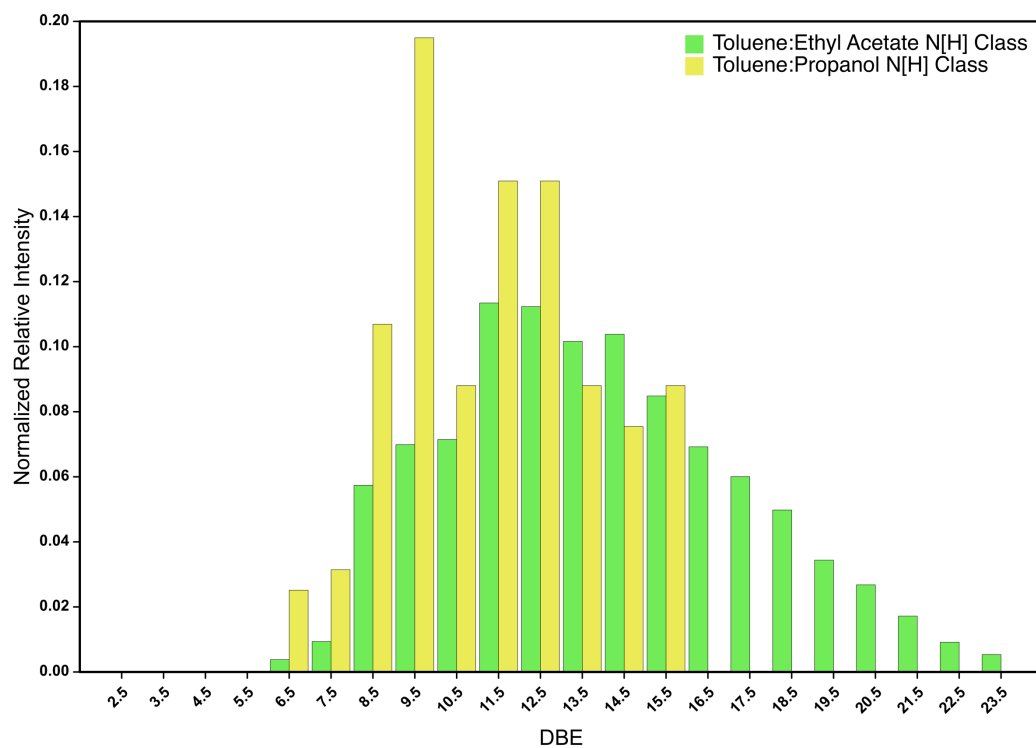
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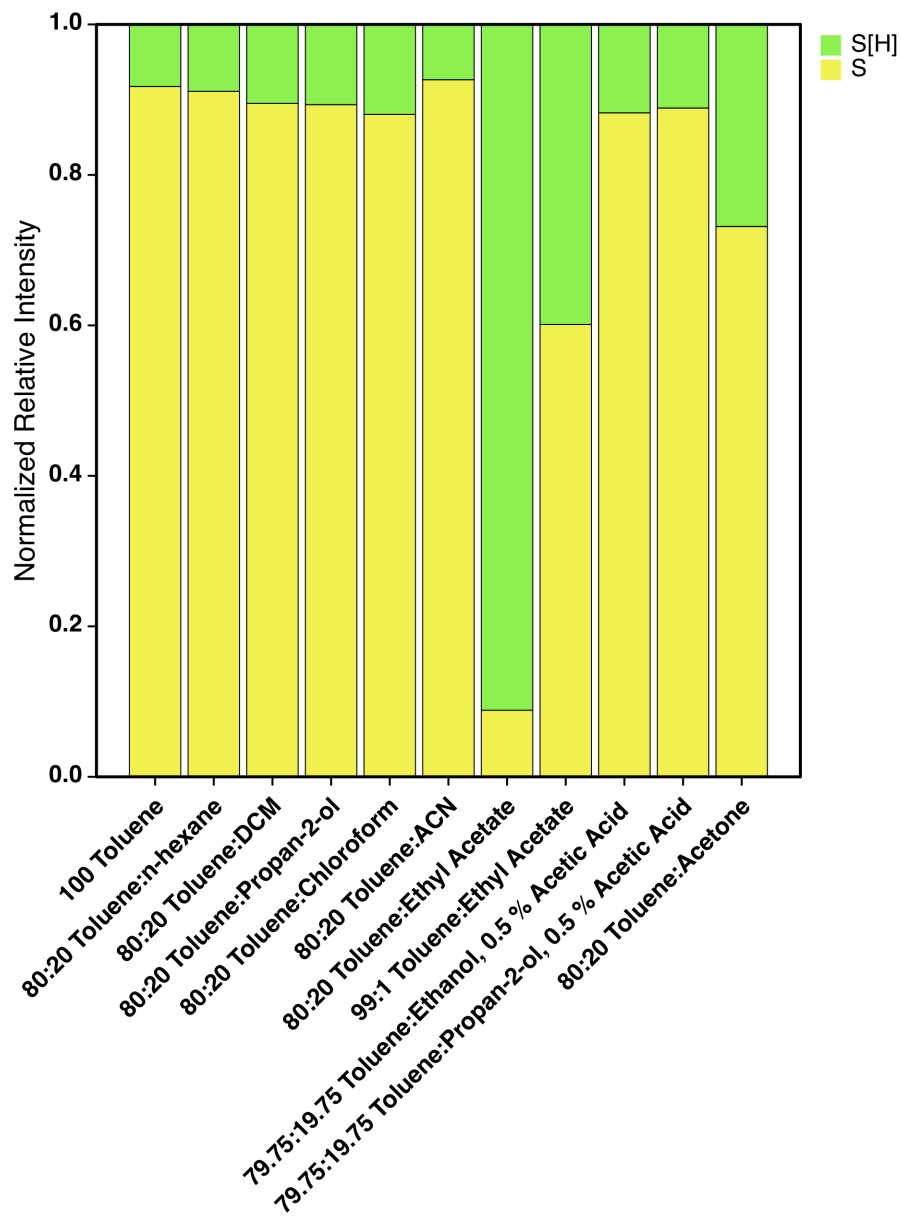
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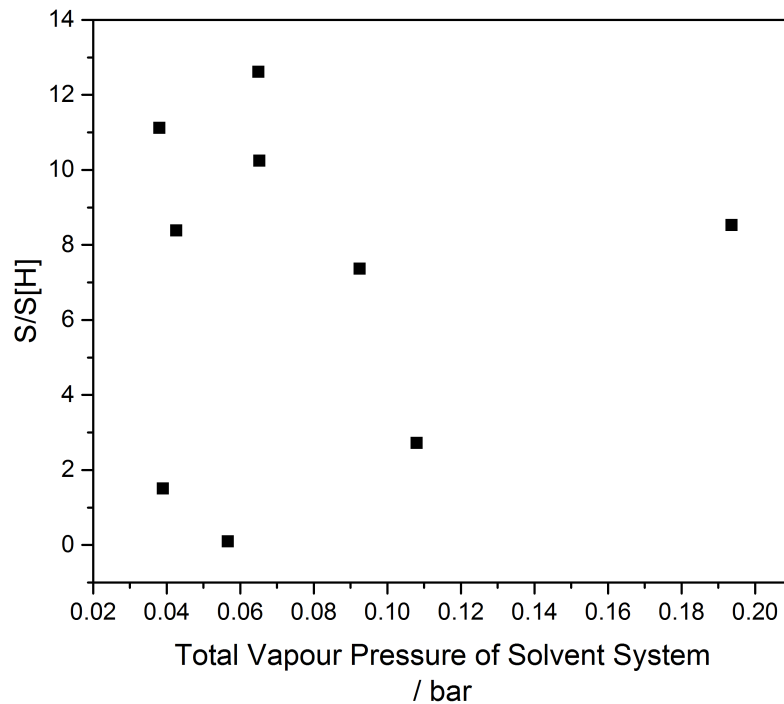
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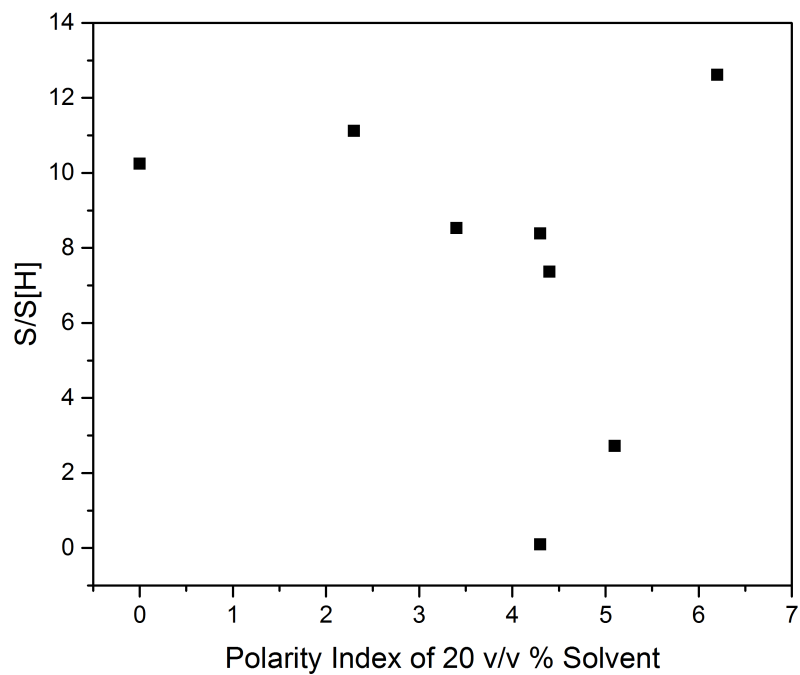
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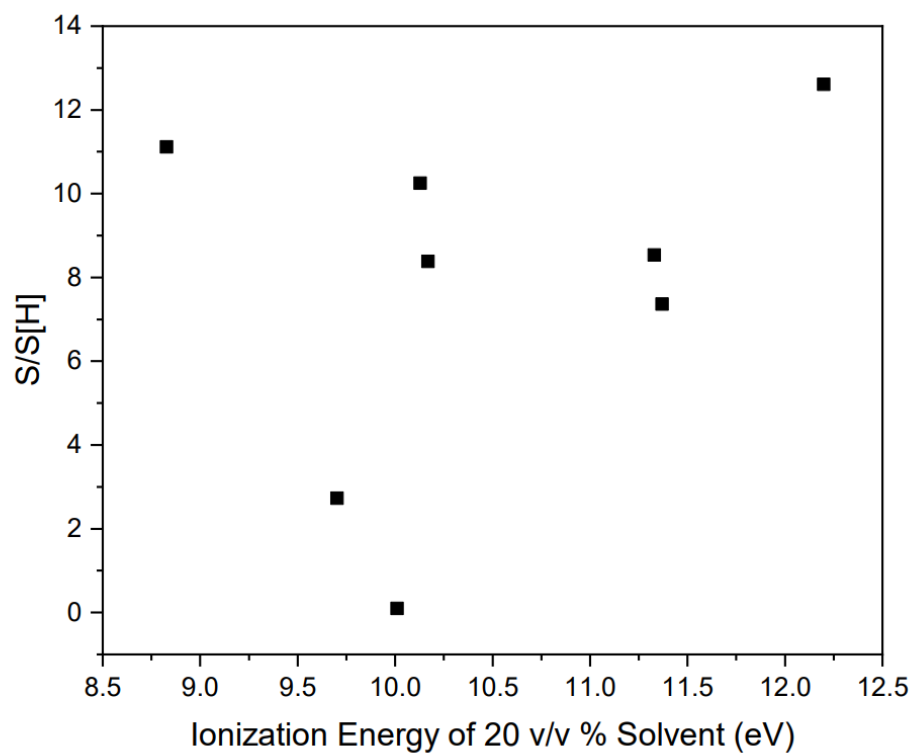
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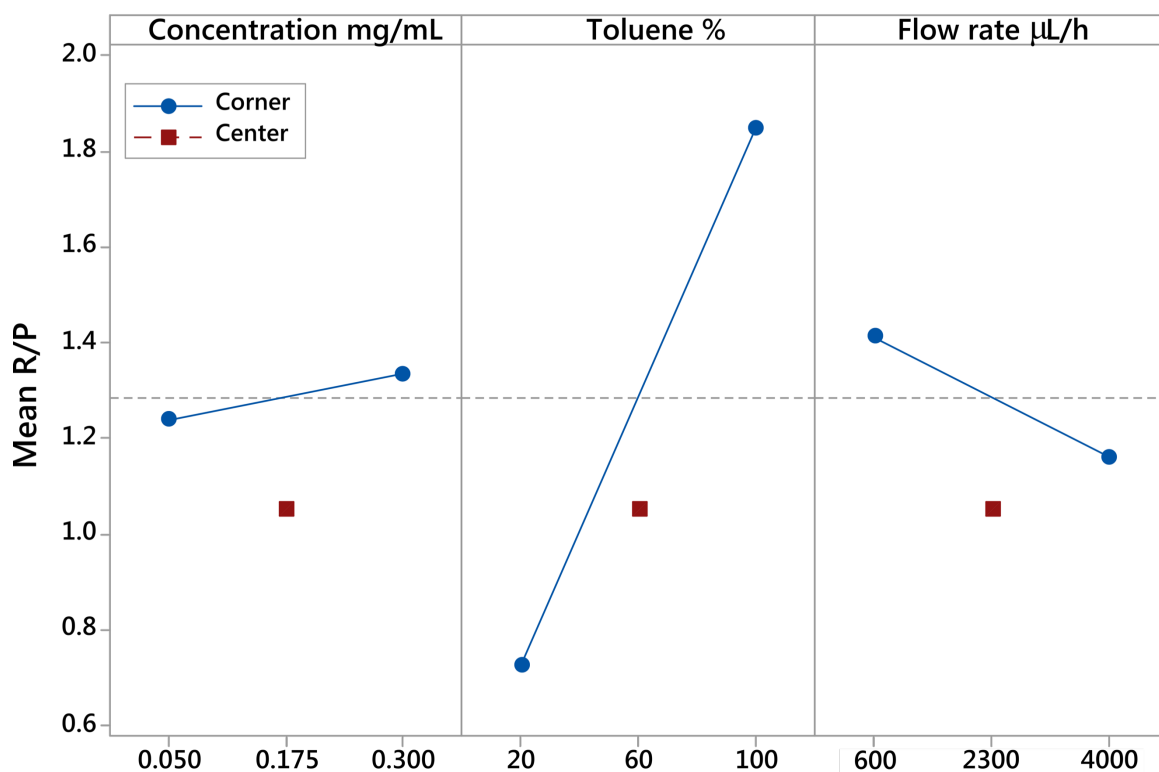
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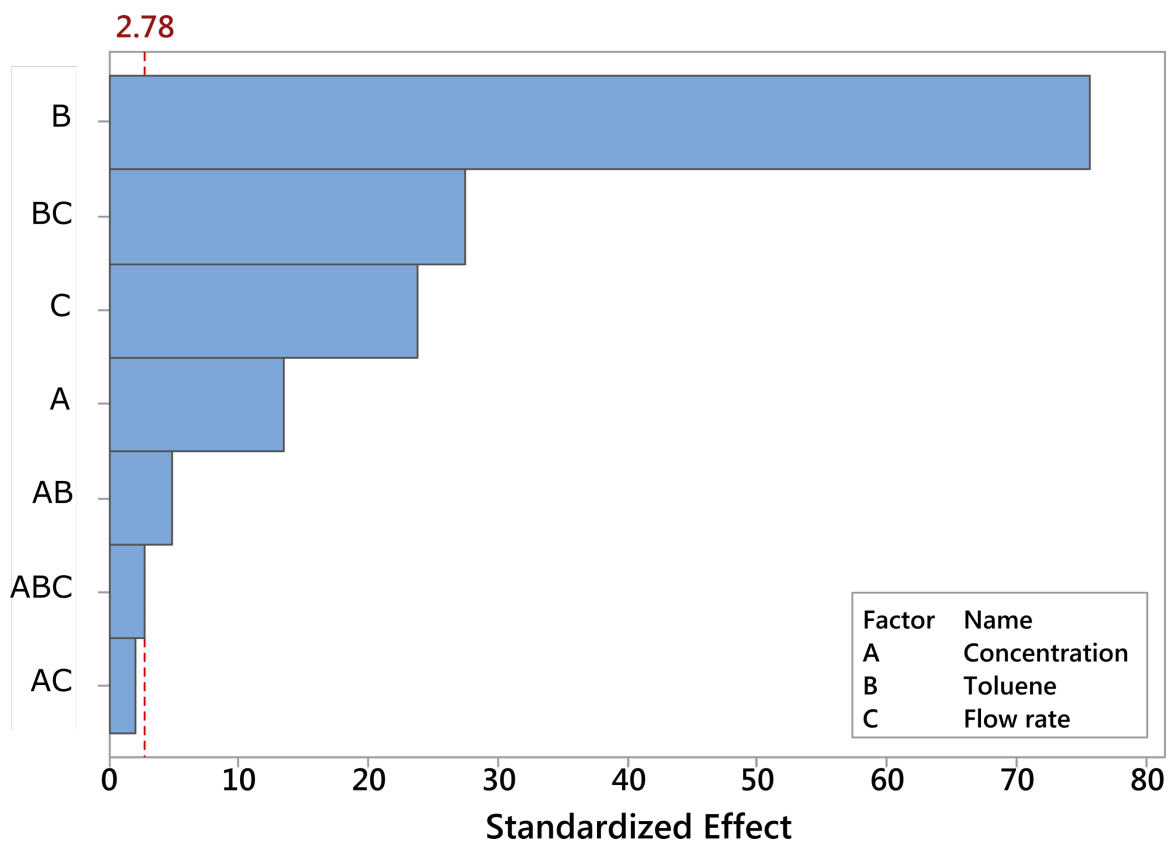
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Molecular entity	Proton Affinity / kJ mol <sup>-1</sup>
Helium	177.8
Argon	369.2
Hydrogen fluoride	484.0
Nitric oxide	531.8
Carbon dioxide	540.5
Methane	543.5
Hydrogen chloride	556.9
Chlorotrifluoromethane	571.3
Ethane	596.3

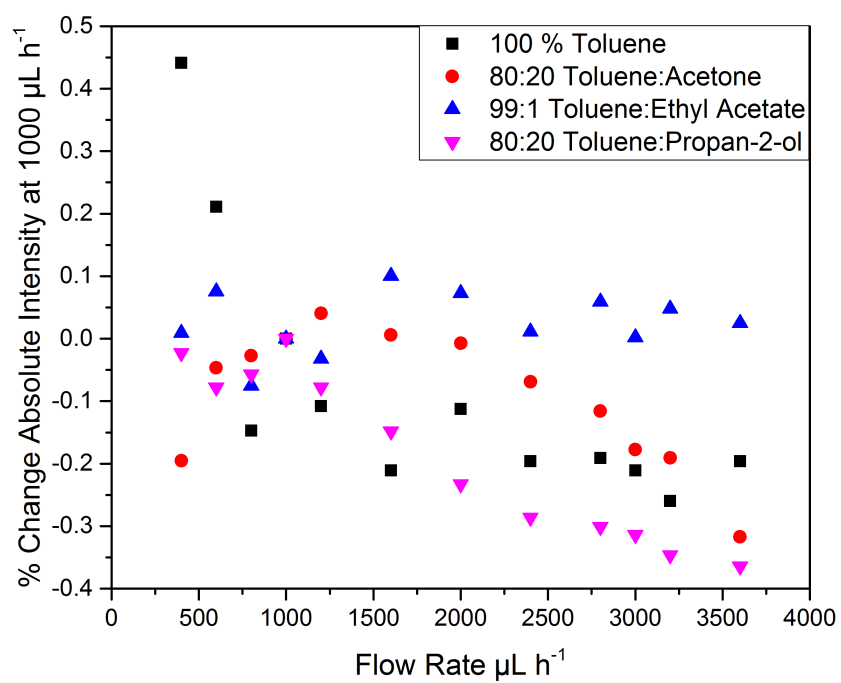


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