Computer-Aided Design of Membrane-Free Batteries Using Conductor-like Screening Model for Real Solvents

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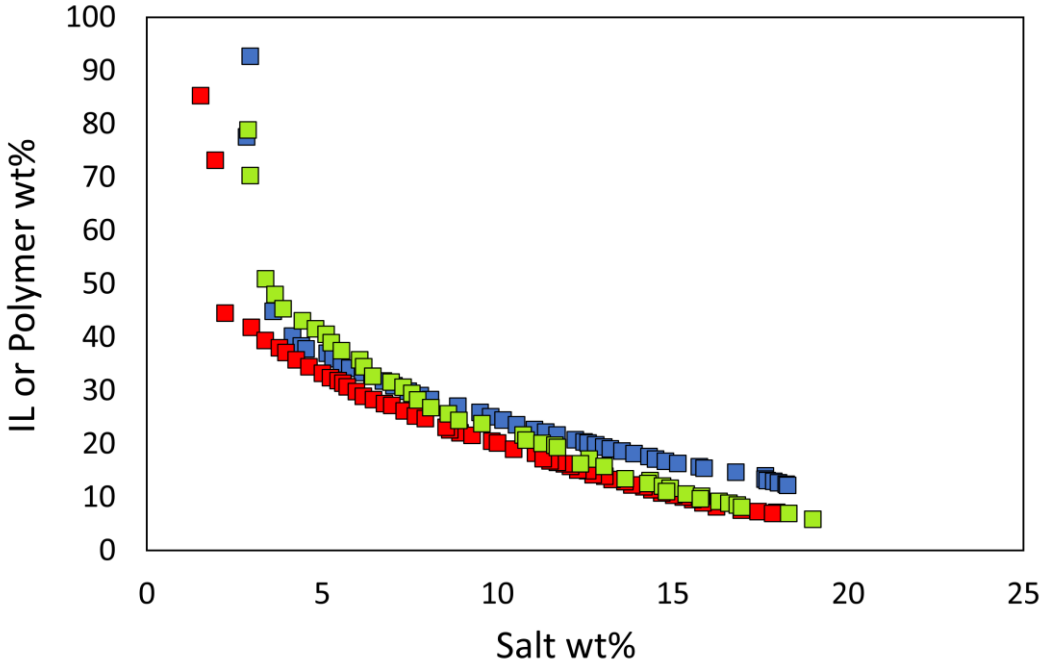

Figure S1 - Phase diagrams in weight percentage shown according at 298±1 K and atmospheric pressure of: green ([P_{44414}]Cl), blue ($PEGDME_{250}$) and red ($PEGDME_{500}$) with $(NH_4)_2SO_4$ and water.

Table S1 - Experimental weight fraction data for the ABS composed of Polymer/IL (1) + $(NH_4)_2SO_4$ (2) + H_2O (3) at (298.15 K) and atmospheric pressure [a].

PEGDME 250		PEGDME 500		[P_{44414}]Cl	
100 w1	**100 w2**	**100 w1**	**100 w2**	**100 w1**	**100 w2**
92.667	2.953	85.279	1.533	78.861	2.890
77.526	2.844	73.175	1.950	70.304	2.951
44.863	3.604	44.509	2.235	50.906	3.385
40.207	4.160	41.843	2.978	48.022	3.662
38.341	4.404	39.363	3.377	45.300	3.890
37.803	4.539	38.010	3.785	43.069	4.441
36.993	5.152	37.105	3.974	41.562	4.810
35.936	5.309	35.770	4.265	40.525	5.112
35.028	5.557	34.476	4.629	38.992	5.259
34.148	5.788	33.214	5.013	37.487	5.550
33.388	6.159	32.403	5.245	35.741	6.072
32.637	6.430	31.853	5.461	34.419	6.186
31.764	6.747	31.355	5.599	32.642	6.449
30.902	7.050	30.667	5.719	31.609	6.967
29.886	7.461	29.819	5.975	30.595	7.307
29.026	7.804	28.922	6.175	29.446	7.560
28.296	8.089	28.266	6.464	28.213	7.732
27.069	8.873	27.562	6.784	26.819	8.099

PEGDME 250		PEGDME 500		$[P_{44414}]Cl$	
100 w1	**100 w2**	**100 w1**	**100 w2**	**100 w1**	**100 w2**
25.888	9.503	27.197	6.990	25.596	8.598
25.058	9.807	26.193	7.339	24.372	8.905
24.429	10.165	25.239	7.667	23.763	9.558
23.585	10.548	24.729	7.943	21.670	10.733
22.665	11.056	22.082	8.939	20.696	10.819
22.221	11.376	21.597	9.280	20.083	11.279
21.642	11.702	20.493	9.838	19.763	11.639
20.750	12.219	20.121	10.006	19.336	11.711
20.377	12.467	19.012	10.466	17.148	12.621
20.141	12.587	18.222	11.092	16.243	12.365
19.803	12.801	7.541	16.959	15.742	13.043
19.394	13.029	7.267	17.433	13.454	13.650
19.064	13.224	7.137	17.963	13.075	14.354
18.676	13.551	6.953	17.853	12.526	14.289
18.172	13.901	4.449	36.294	12.099	14.712
17.593	14.326	8.173	16.250	11.686	14.930
17.172	14.506	8.940	15.859	11.037	14.823
16.753	14.794	9.521	15.569	10.551	15.385
16.349	15.149	10.047	15.299	10.169	15.822
15.694	15.757	10.343	15.036	9.650	15.791
15.396	15.890	10.762	14.692	9.217	16.325
14.672	16.795	11.381	14.404	8.858	16.605
13.998	17.639	11.948	14.174	8.509	16.837
13.365	17.627	12.257	13.830	8.115	16.961
13.135	17.697	12.871	13.637	6.955	18.312
12.946	17.879	13.283	13.271	5.845	18.992
12.680	18.019	13.937	13.069		
12.385	18.237	14.210	12.732		
12.187	18.281	14.942	12.575		
		15.069	12.294		
		15.759	12.086		
		16.239	11.913		
		16.520	11.709		
		16.805	11.502		
		17.179	11.306		

[a] Standard uncertainty u are u(w) = 0.001, u(T) = 0.5 K, and u(P) = 10 kPa.

Table S2 - Parameters A, B and C obtained from Merchuck fitting [1] for each ABS tested, with ammonium sulphate and water.

IL/Pol	A ± σ	B ± σ	10^5 (C ± σ)	R^2
PEGDME 250	65.119 ± 14.275	-0.353 ± 0.058	0.818 ± 0.370	0.98
PEGDME 500	70.457 ± 12.618	-0.461 ± 0.053	-0.077 ± 0.292	0.91
$[P_{44414}]Cl$	248.934 ± 56.767	-0.789 ± 0.109	0.177 ± 7.147	0.96

Table S3 - TLs weight fraction composition of IL/Pol (1) + $(NH_4)_2SO_4$ (2) aqueous biphasic systems.

Mixture Point*	IL/Pol	Weight fraction composition (wt%)					
		[IL/Pol]'	[Salt]'	[IL/Pol]''	[Salt]''	TLL	α
1	PEGDME 250	56.459	1.031	1.872	40.198	67.18	0.486
	PEGDME 500	55.454	2.553	1.570	39.546	65.36	0.473
	$[P_{44414}]Cl$	57.486	3.446	3.332	29.262	59.99	0.545
2	PEGDME 250	51.779	1.371	2.480	37.300	61.03	0.381
	PEGDME 500	53.389	2.462	2.495	33.997	59.87	0.401
	$[P_{44414}]Cl$	71.812	2.480	2.816	31.442	74.83	0.395

* 1, used in Section 3.2: 33% wt (IL/Pol), 15% wt (Salt); 2 used in Section 3.3: 30% wt (IL/Pol), 20% wt (Salt)

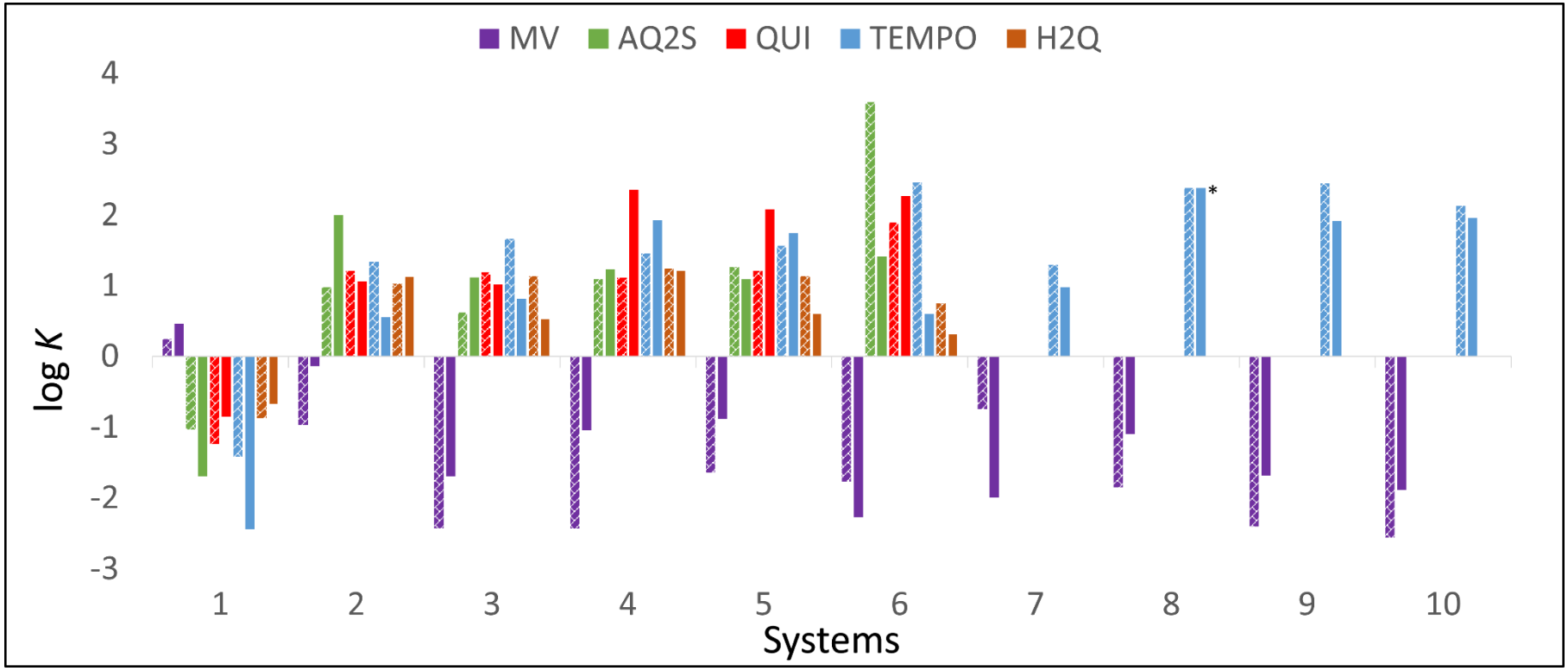

Figure S2: Comparison between experimental and calculated values for log of partition coefficients (K) of redox molecules in different ABS. Full color: experimental data [2–4] diagonal brick: predicted by COSMO-RS in this work. *Measured in this work at the same mixture point described by Navalpotro et l [4]

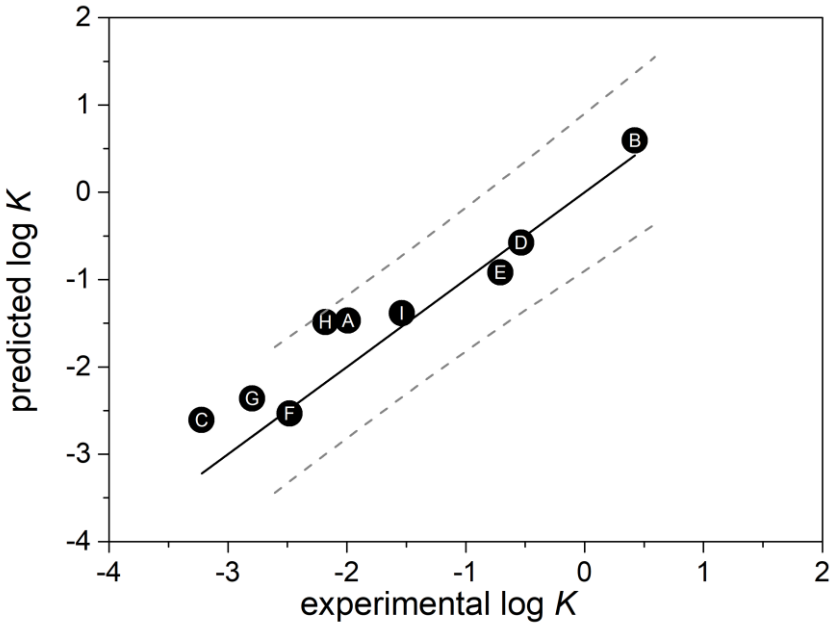

Figure S3 - Experimental vs predicted log of *K* for System 1: PEGDME250+ $(NH_4)_2SO_4$ + water, for the synthesized viologen derivatives (A,B, C-Cl, D-Br, E-Br, F-Br, G-Cl, H-Cl, I-Br). Perfect prediction (full line) and, 95% prediction intervals (dashed lines).

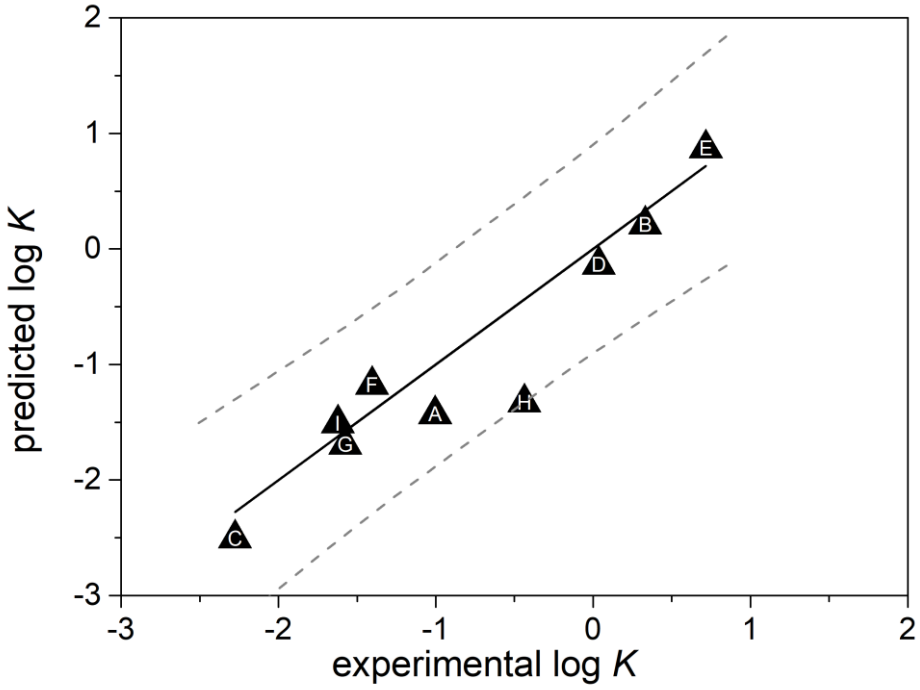

Figure S4 - Experimental vs predicted log of *K* for System 2: PEGDME500+ $(NH_4)_2SO_4$ + water, for the synthesized viologen derivatives (A,B, C-Cl, D-Br, E-Br, F-Br, G-Cl, H-Cl, I-Br). Perfect prediction (full line) and, 95% prediction intervals (dashed lines).

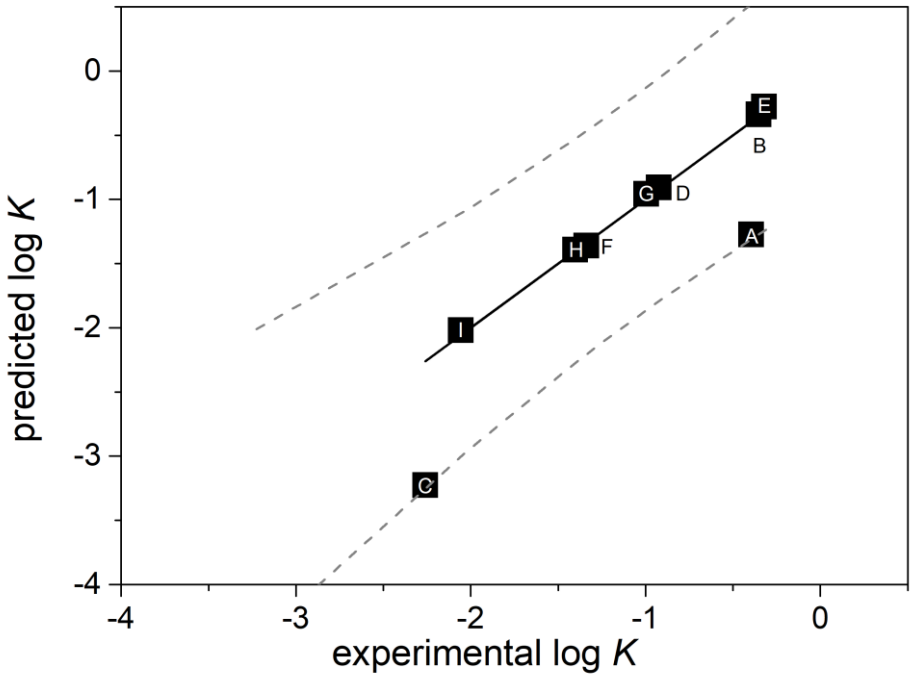

Figure S5 - Experimental vs predicted log of *K* for System 3: $[P_{44414}]Cl + (NH_4)_2SO_4$ + water, for the synthesized viologen derivatives (A,B, C-Cl, D-Br, E-Br, F-Br, G-Cl, H-Cl, I-Br). Perfect prediction (full line) and, 95% prediction intervals (dashed lines).

The experimental results for System PEGDME250+ $(NH_4)_2SO_4$ + water suggest that most of the tested viologen derivatives have a greater preference for the salt-rich phase, except for viologen B which is more concentrated in the polymer phase (as shown in Figure S6. These findings are consistent with the σ-profiles presented in Figure 3 (manuscript), which indicate the highly hydrophilic nature of the viologen derivatives. The Pearson correlation between the predicted and experimental values was exceptional, with a value of 0.97.

As well, for System PEGDME500+ $(NH_4)_2SO_4$ + water, COSMO-RS predictions showed good agreement with the experimental data, with a Pearson correlation coefficient of 0.93 (Figure S4). It is important to note that for polymer modeling, the complete structures of the polymers were optimized, starting from the monomer and replicating it to achieve the desired final molar weight of 250 or 500 g/mol.

Figure S5 in the Supporting Information shows the individual results of System $[P_{44414}]Cl + (NH_4)_2SO_4$ + water. However, the predicted *K* value for viologen A was overestimated, which impacted the correlation coefficient (r = 0.83). This could be attributed to the notable highly hydrophilic character of viologen A.

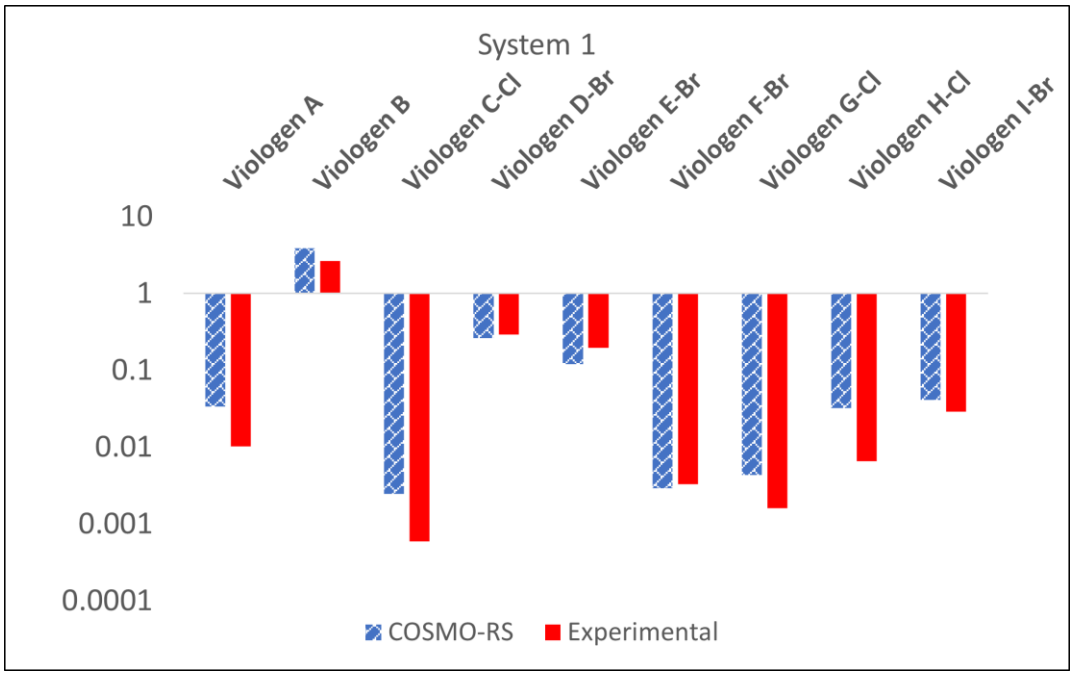

Figure S6 - Comparison between experimental and calculated values for log *K* of several viologen derivatives in $PEGDME_{250}$ + $(NH_4)_2SO_4$ and water

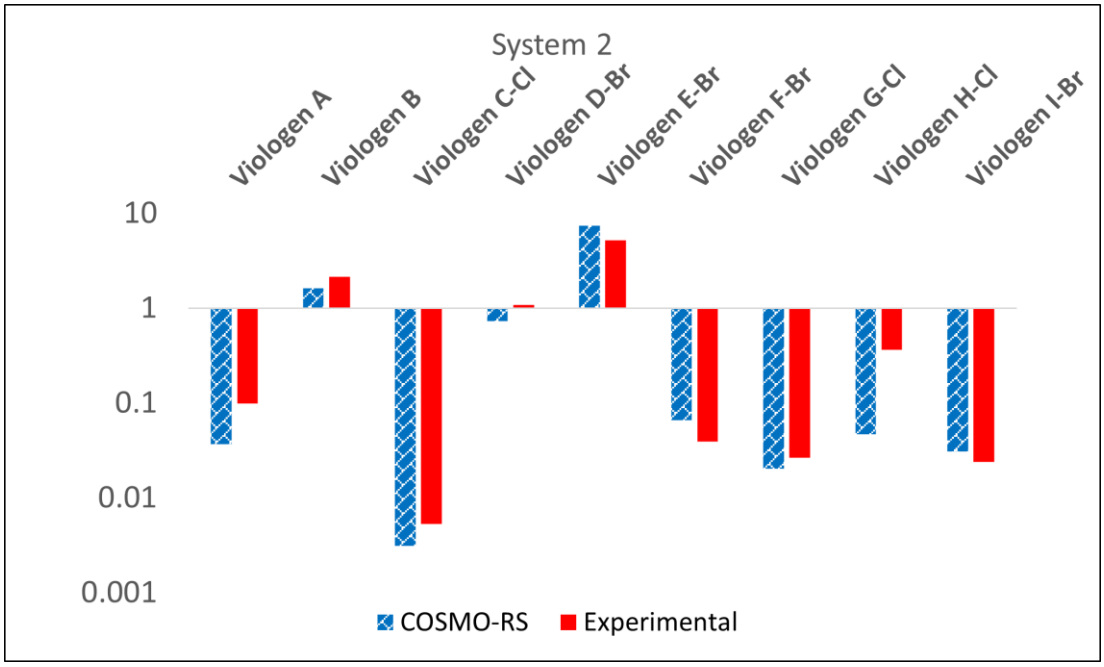

Figure S7 - Comparison between experimental and calculated values for log *K* of several viologen derivatives in $PEGDME_{500}$ + $(NH4)_2SO_4$ and water

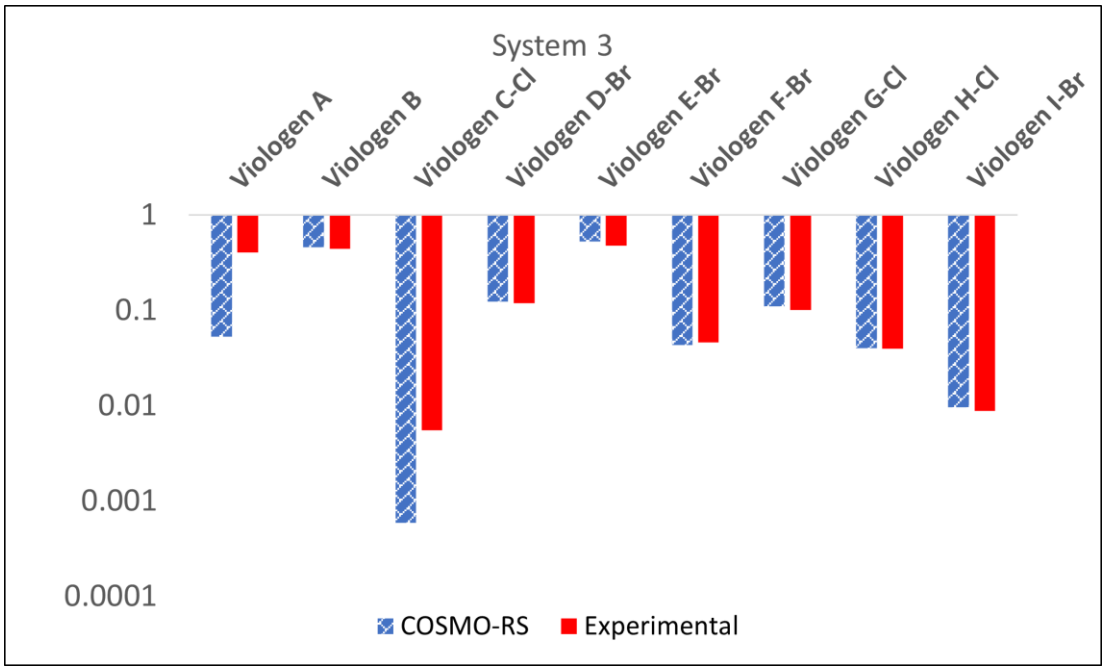

Figure S8 - Comparison between experimental and calculated values for log *K* of several viologen derivatives in $[P_{44414}]Cl + (NH_4)_2SO_4$ and water

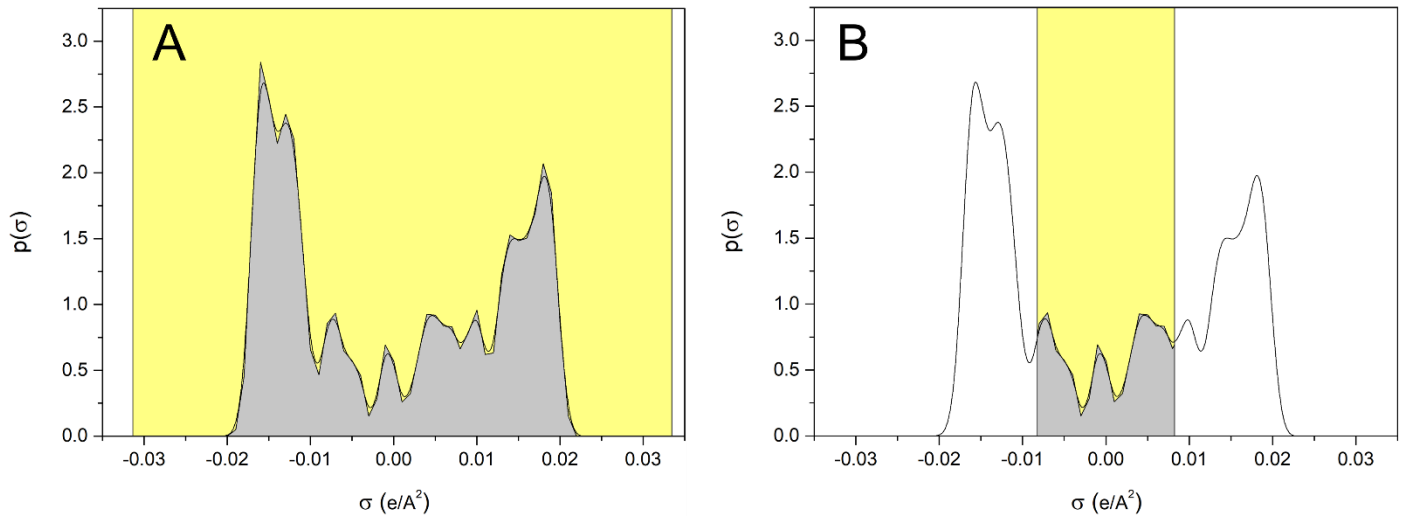

Figure S9 – Total area of the σ-profile (A) and non-polar area (B) of a compound.

After defining the total area below the σ-profile curve, Figure S9 (A), and the apolar area Figure S4 (B) the overall polarity of the compound can be calculated according to the following equation.

$$\%polarity = \frac{(area_{total} - area_{non-polar})}{area\_total}.100$$

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