Supporting Information

Solvent screening for the purification of monoterpenoids by countercurrent and centrifugal partition chromatography

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Table S1. Physicochemical properties of the selected monoterpenoids.

Monoterpenoid	Melting point (K)[a]	Normal boiling point (K)	Density ($kg \cdot m^{-3}$)	Dynamic viscosity (mPa·s)	Surface tension ($mN \cdot m^{-1}$)
(S)-(+)-carvone	246.7 ± 0.3[1]	502.2[2,b]	957.5[3,c]	4.38[4,c,d]	34.2[5,c,d]
Eucalyptol	274.1 ± 0.3[6]	449.2[7]	920.2[8,c]	2.64[8,c]	25.7[8,c]
Thymol	322.0 ± 0.1[9]	505.2[10,11]	942.2[3,e]	-	-

[a]Data measured reported at p = 1 bar.
[b]No information regarding the main isomeric form.
[c]Data measured at T = 298.2 K.
[b]Data reported for l-carvone.
[e]Data measured at T = 333.2 K.

Experimental analytical methods

Ultraviolet-visible (UV-Vis) spectroscopy

The partition coefficients of thymol were determined by UV-Vis analysis (T70, P.G. Instruments) since this compound has a substantial response in the ultra-violet region. The measurements were performed using semi-micro cuvettes of optical paths of 10 mm (cuvettes volume of 1.5 cm^3, ethanol as the solvent, at the wavelength of 277 nm) or 50 mm (cuvette volume of 7 cm^3, ethanol/water (wt% 50/50) as a solvent, at the wavelength of 275.5 nm). The concentration of the solute in each phase was obtained using calibration curves (R^2 > 0.9997) built with at least 7 independent standards. Two independent measurements were performed for each sample collected from the shake flask tubes.

Gas-chromatography (GC)

The partition coefficients of carvone and eucalyptol were determined by GC analysis since these compounds have no significant response in the UV-Vis region. Experiments were conducted in a GC-FID (CP3800, Varian) equipped split/spitless injection system and fitted with a SUPELCOWAX® 10 capillary column (L x I.D. 30 m x 0.25 mm, df 0.25 μm). To perform the experiments, helium was used at the carrier gas (1.2 $ml \cdot min^{-1}$), the injection volume was 2 μl with a split ratio of 1:2, the injector and detector were kept at 523.2 K, and the oven temperature was initially set at 373.2 K and held at this temperature time intervals up to 35 min, increased up to 503.2 K at 65 $K \cdot min^{-1}$ and held at 503.2 K for 5 minutes. The solute concentration in each phase was determined by the internal-standard method, using (±)-linalool as the internal standard. For each solute, calibration curves (R^2 > 0.9995) were built using at least 7 independent standards.

Table S2. Proportions (in volume basis) of the quaternary solvent systems studied in this work.

Solvent system	**Volumetric proportion**					
	Heptane	*R*(+)-Limonene	Ethyl acetate	Methanol	Ethanol	Water
Arizona N	1	-	1	1	-	1
Arizona T	3	-	1	3	-	1
Modified Arizona N	1	-	1	-	1	1
Modified Arizona T	1	-	1	-	3	1
Green Arizona N	-	1	1	-	1	1
Green Arizona T	-	3	1	-	3	1

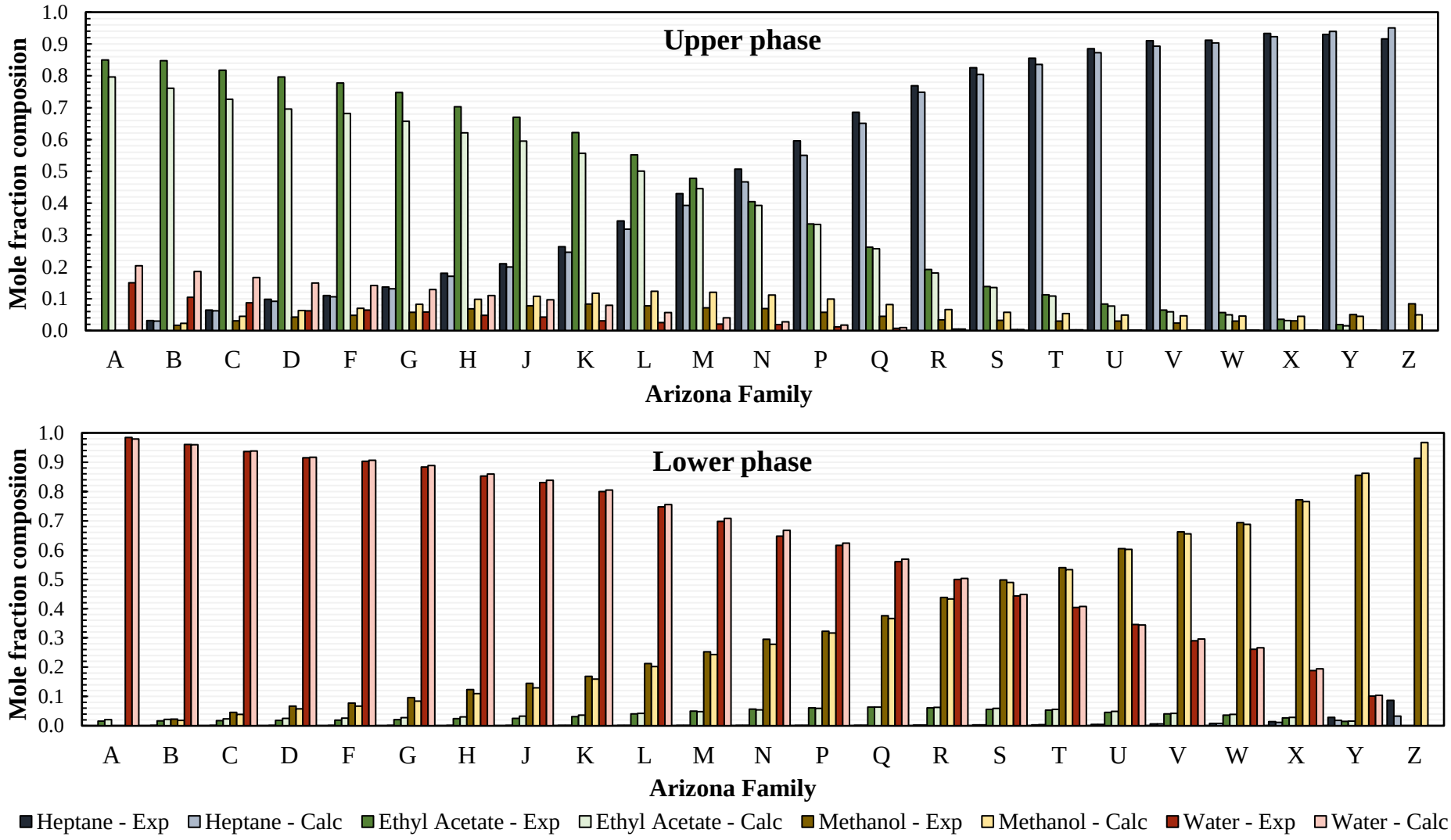

Figure S1. Comparison between the experimental[12] phase composition of the Original Arizona solvent systems with the values predicted with COSMO-RS, at 295.2 K.

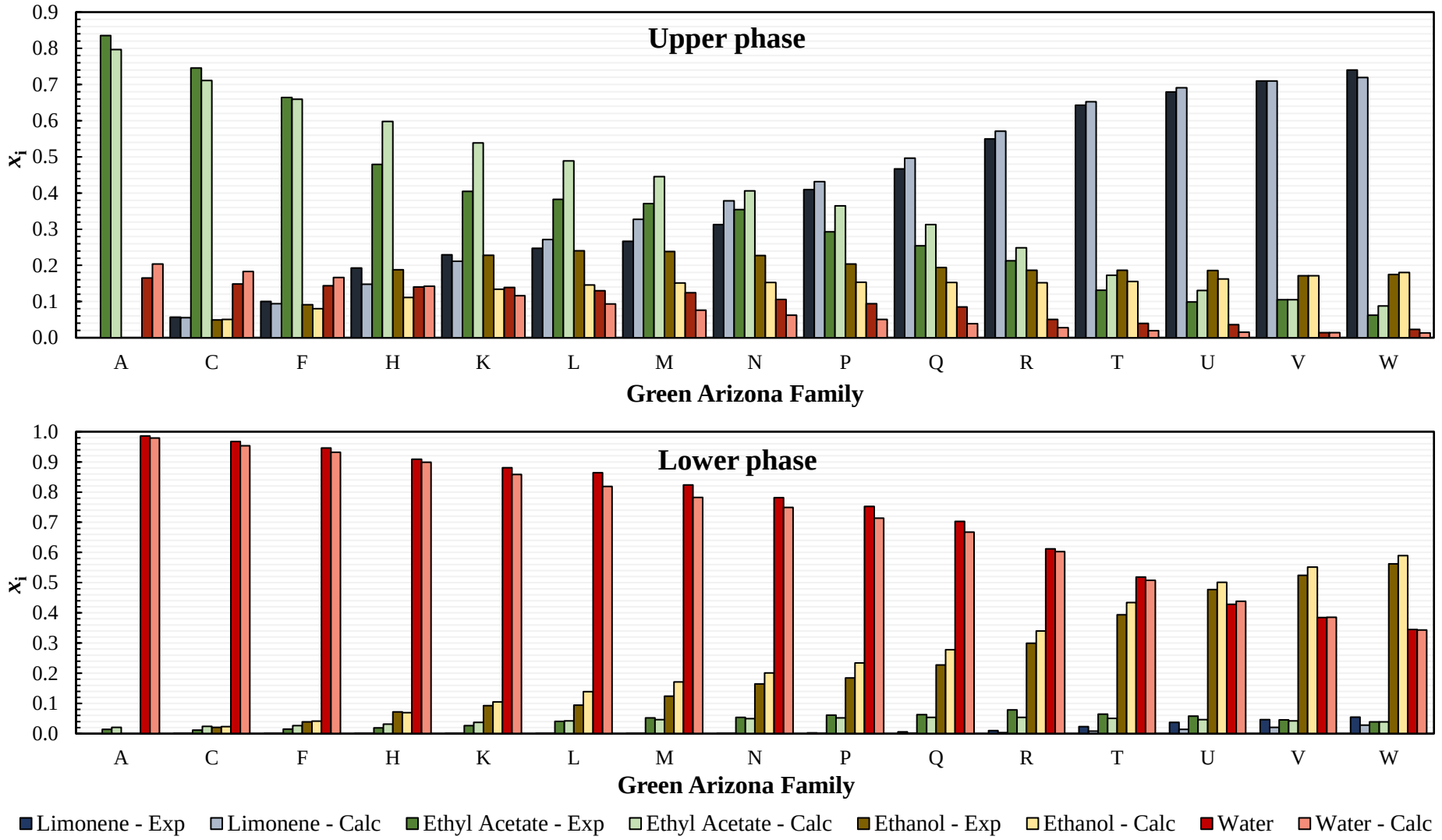

Figure S2. Comparison between the experimental[13] phase composition of the Green Arizona solvent systems with the values predicted with COSMO-RS, at 295.2 K

Table S3. Overview of the global compositions of the Original Arizona system.

Solvent system	Volume basis[12]				Mole fraction basis			
	methanol	ethyl acetate	heptane	water	methanol	ethyl acetate	heptane	water
A	0.00	2.00	0.00	2.00	0.0000	0.1550	0.0000	0.8450
B	0.10	1.90	0.10	1.90	0.0192	0.1512	0.0053	0.8242
C	0.20	1.80	0.20	1.80	0.0395	0.1472	0.0109	0.8023
D	0.29	1.71	0.29	1.71	0.0588	0.1434	0.0162	0.7816
F	0.33	1.67	0.33	1.67	0.0677	0.1416	0.0187	0.7720
G	0.40	1.60	0.40	1.60	0.0837	0.1385	0.0231	0.7547
H	0.50	1.50	0.50	1.50	0.1077	0.1337	0.0298	0.7288
J	0.57	1.43	0.57	1.43	0.1255	0.1302	0.0347	0.7097
K	0.67	1.33	0.67	1.33	0.1521	0.1249	0.0420	0.6809
L	0.80	1.20	0.80	1.20	0.1894	0.1175	0.0524	0.6407
M	0.91	1.09	0.91	1.09	0.2236	0.1108	0.0618	0.6038
N	1.00	1.00	1.00	1.00	0.2535	0.1049	0.0701	0.5716
P	1.09	0.91	1.09	0.91	0.2854	0.0986	0.0789	0.5372
Q	1.20	0.80	1.20	0.80	0.3273	0.0903	0.0905	0.4920
R	1.33	0.67	1.33	0.67	0.3816	0.0795	0.1055	0.4334
S	1.43	0.57	1.43	0.57	0.4274	0.0705	0.1181	0.3841
T	1.50	0.50	1.50	0.50	0.4617	0.0637	0.1276	0.3470
U	1.60	0.40	1.60	0.40	0.5145	0.0532	0.1422	0.2900
V	1.67	0.33	1.67	0.33	0.5544	0.0453	0.1532	0.2470
W	1.71	0.29	1.71	0.29	0.5784	0.0406	0.1598	0.2212
X	1.80	0.20	1.80	0.20	0.6358	0.0292	0.1757	0.1593
Y	1.90	0.10	1.90	0.10	0.7058	0.0154	0.1951	0.0838
Z	2.00	0.00	2.00	0.00	0.7835	0.0000	0.2165	0.0000

Table S4. Overview of the global compositions of the Green Arizona system.

Solvent system	Volume basis[13]				Mole fraction basis			
	ethanol	ethyl acetate	limonene	water	ethanol	ethyl acetate	limonene	water
A	0.00	2.00	0.00	2.00	0.0000	0.1550	0.0000	0.8450
C	0.20	1.80	0.20	1.80	0.0278	0.1492	0.0101	0.8130
F	0.33	1.67	0.33	1.67	0.0486	0.1448	0.0176	0.7891
H	0.50	1.50	0.50	1.50	0.0775	0.1387	0.0281	0.7557
K	0.67	1.33	0.67	1.33	0.1105	0.1317	0.0400	0.7178
L	0.80	1.20	0.80	1.20	0.1403	0.1254	0.0508	0.6835
M	0.91	1.09	0.91	1.09	0.1673	0.1197	0.0606	0.6523
N	1.00	1.00	1.00	1.00	0.1920	0.1145	0.0696	0.6239
P	1.09	0.91	1.09	0.91	0.2190	0.1088	0.0794	0.5929
Q	1.20	0.80	1.20	0.80	0.2547	0.1012	0.0923	0.5517
R	1.33	0.67	1.33	0.67	0.3044	0.0907	0.1103	0.4945
T	1.50	0.50	1.50	0.50	0.3782	0.0752	0.1371	0.4096
U	1.60	0.40	1.60	0.40	0.4304	0.0641	0.1560	0.3496
V	1.67	0.33	1.67	0.33	0.4692	0.0559	0.1700	0.3049
W	1.71	0.29	1.71	0.29	0.4992	0.0496	0.1809	0.2703

Table S5. Overview of the global compositions of the proposed Modified Arizona system.

Solvent system	Volume basis				Mole fraction basis			
	ethanol	ethyl acetate	heptane	water	ethanol	ethyl acetate	heptane	water
A	0.00	2.00	0.00	2.00	0.0000	0.1550	0.0000	0.8450
B	0.10	1.90	0.10	1.90	0.0134	0.1521	0.0053	0.8291
C	0.20	1.80	0.20	1.80	0.0278	0.1490	0.0111	0.8122
D	0.29	1.71	0.29	1.71	0.0409	0.1462	0.0163	0.7967
F	0.33	1.67	0.33	1.67	0.0485	0.1445	0.0193	0.7877
G	0.40	1.60	0.40	1.60	0.0596	0.1421	0.0237	0.7746
H	0.50	1.50	0.50	1.50	0.0773	0.1383	0.0308	0.7536
J	0.57	1.43	0.57	1.43	0.0908	0.1353	0.0362	0.7377
K	0.67	1.33	0.67	1.33	0.1100	0.1312	0.0438	0.7150
L	0.80	1.20	0.80	1.20	0.1396	0.1248	0.0556	0.6801
M	0.91	1.09	0.91	1.09	0.1663	0.1190	0.0662	0.6485
N	1.00	1.00	1.00	1.00	0.1907	0.1137	0.0759	0.6196
P	1.09	0.91	1.09	0.91	0.2173	0.1079	0.0865	0.5883
Q	1.20	0.80	1.20	0.80	0.2524	0.1003	0.1005	0.5467
R	1.33	0.67	1.33	0.67	0.3011	0.0898	0.1199	0.4892
S	1.43	0.57	1.43	0.57	0.3406	0.0812	0.1356	0.4426
T	1.50	0.50	1.50	0.50	0.3732	0.0741	0.1486	0.4041
U	1.60	0.40	1.60	0.40	0.4238	0.0632	0.1688	0.3442
V	1.67	0.33	1.67	0.33	0.4614	0.0550	0.1837	0.2998
W	1.71	0.29	1.71	0.29	0.4904	0.0487	0.1953	0.2656

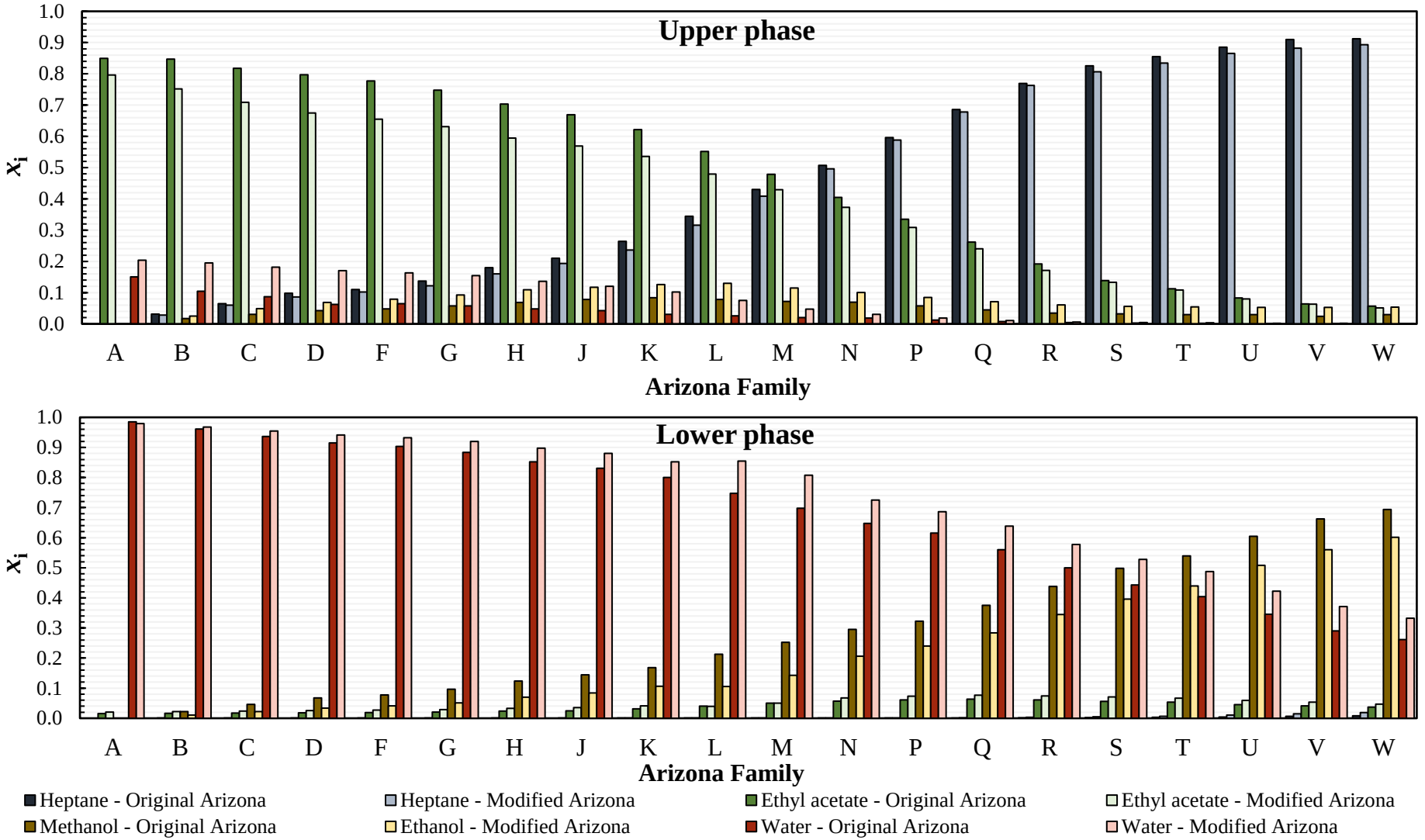

Figure S3. Comparison between the experimental phase compositions of the Original Arizona family[12] with the predicted data for the Modified Arizona systems, at 295.2 K.

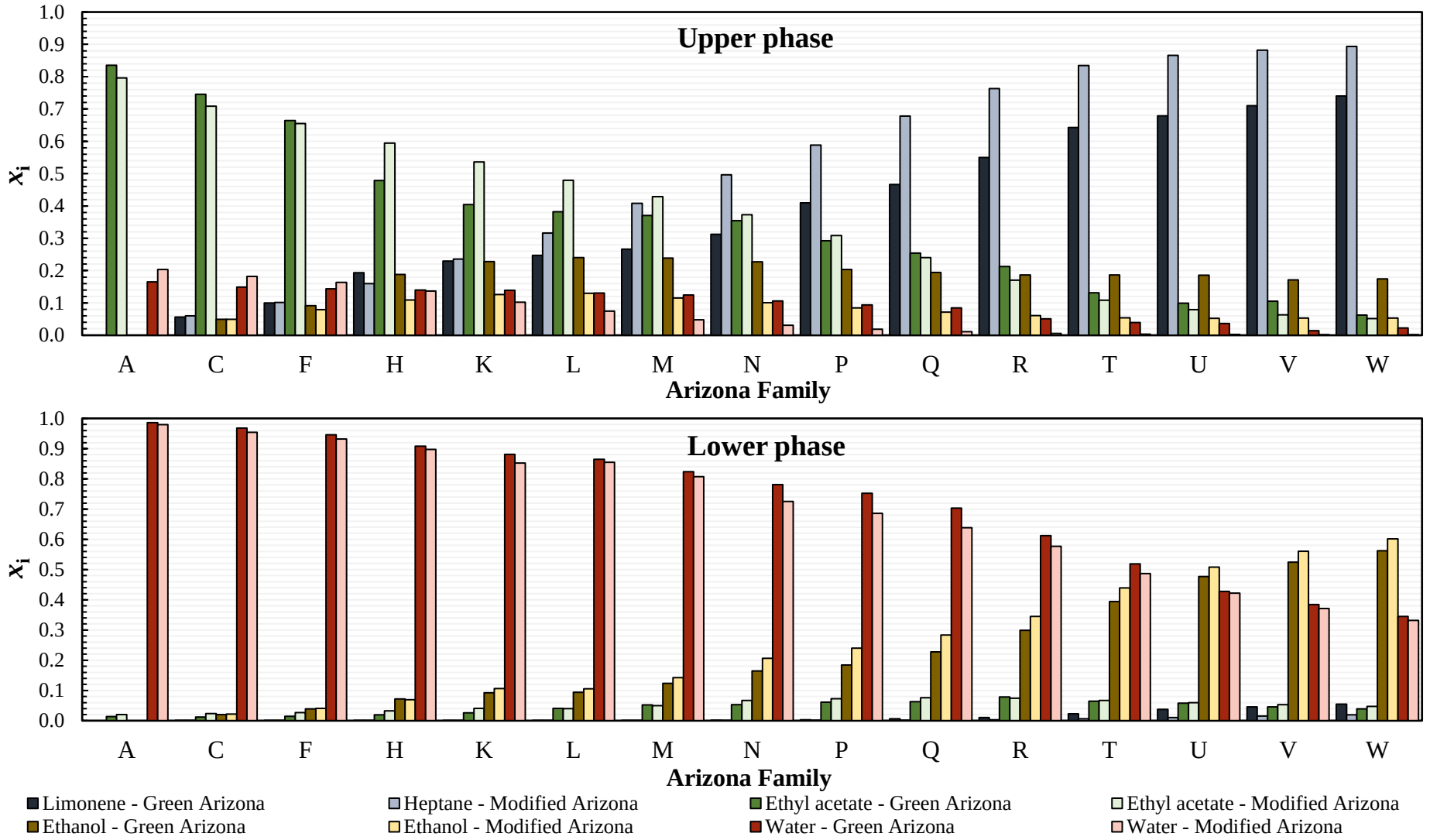

Figure S4. Comparison between the experimental phase compositions of the Green Arizona family[13] with the predicted data for the Modified Arizona systems, at 295.2 K.

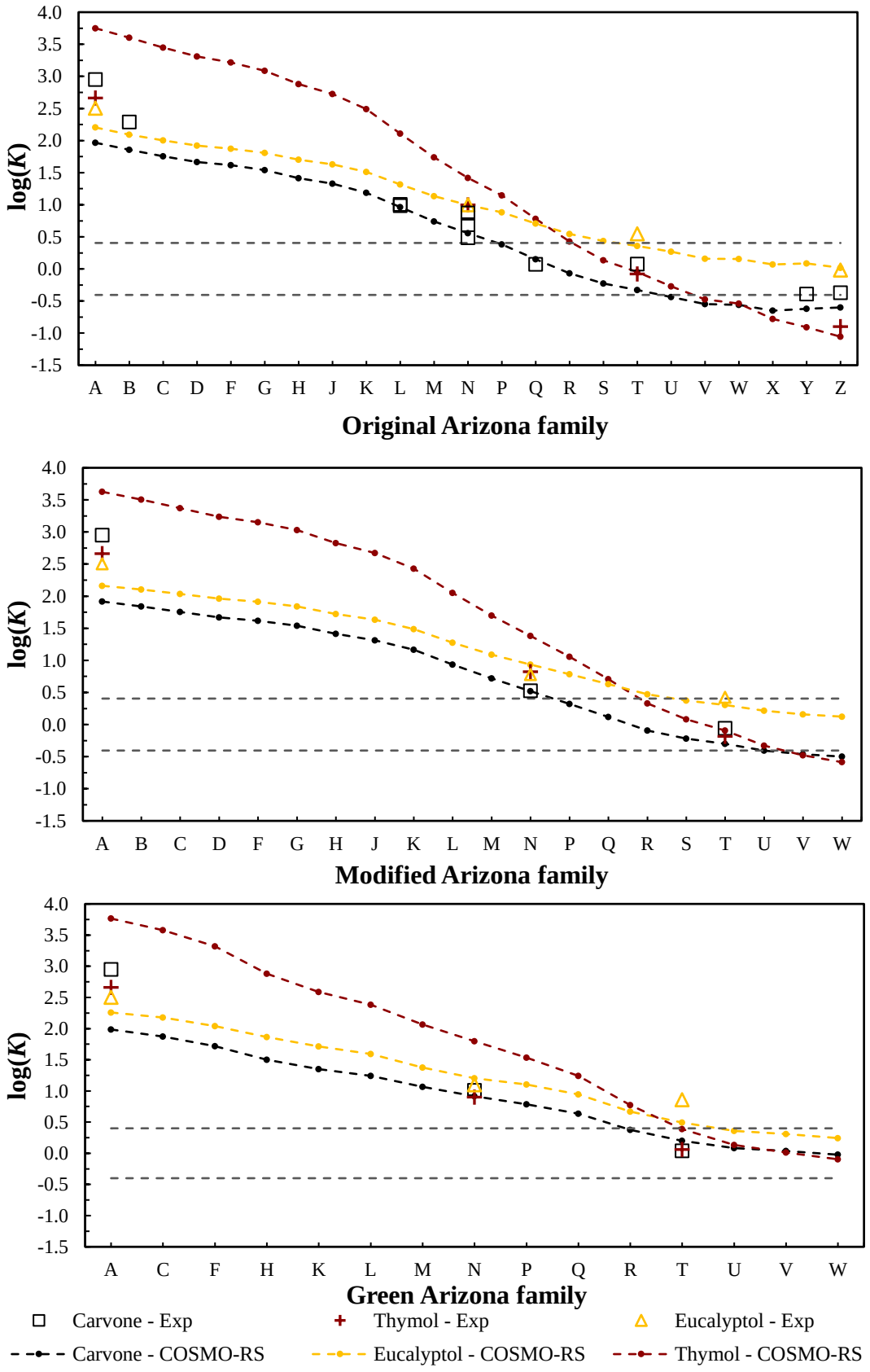

Figure S5. Overview of the experimental (measured in this work and collected from the literature[14–17]) and predicted Log(*K*) values as a function of the solvent systems for the Original Arizona, Modified Arizona, and Green Arizona families. The horizontal gray dashed lines correspond to the sweet-pot polarity region (-0.4 < Log(*K*) < 0.4).[18,19]

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