Electronic Supplementary Material (ESI) for Molecular Systems Design & Engineering.

Supplementary information to

“COSMO-CAMPD: A framework for integrated design of molecules and processes based on COSMO-RS”

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1. Experimental Methods

The measurement setup uses a liquid-handling autosampler, which prepares LLE with a total volume of 1 mL in a temperature-controlled tray and takes samples from the upper and the lower phase after equilibration. The samples are directly injected into a gas chromatograph without dilution nor addition of a standard. A detailed description of the experimental procedure can be found in Dechambre et al. 2014.

Table 1: List of chemicals

	provider	specification	purity (GC, A %)
γ-valerolactone	Sigma-Aldrich	ReagentPlus®	99
water	Merck	SupraSolv®	
toluene	VWR	spectronorm	99.8
2-methylfuran	Sigma-Aldrich		99
n-butyl acetate	Merck	for analysis	99.5

Table 2: Gas chromatography parameters

parameter	value
column	FS-CW20M-CB
carrier gas	He
inlet temperature in K	523.15
split	25:1
p in bar	0.3
T_1 in K	373.15
hold in min	4
T_{ramp} in K min^{-1}	50
T_2 in K	453.15
hold in min	9
detector	TCD/FID
detector temperature in K	523.15/523.15

2. Experimental Results

A comparison of COSMO-RS predictions on TZVP level and TZVPD-FINE level for the investigated solvents n-butyl acetate and toluene are shown in Figure 1.

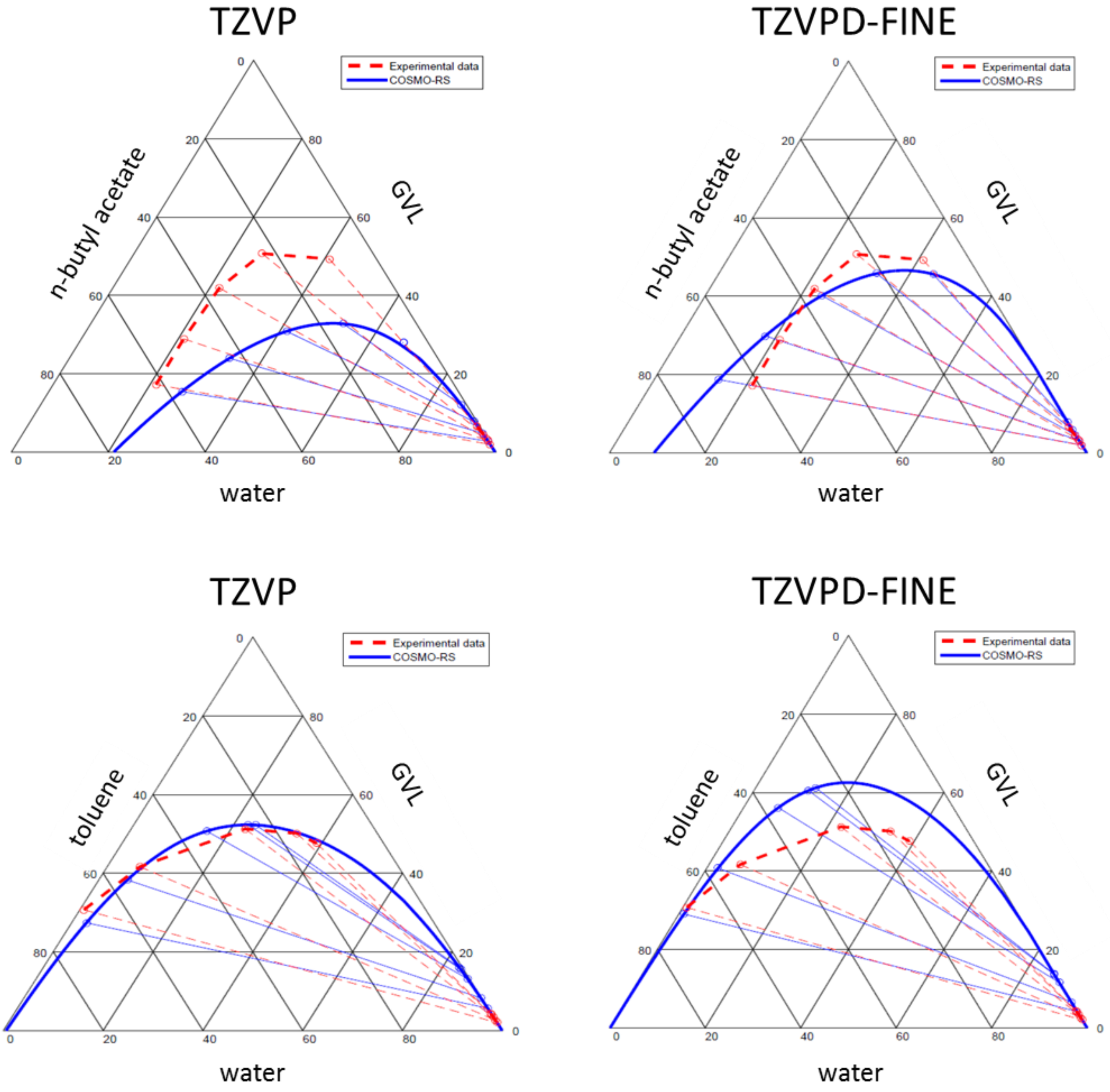

Figure 1: Experimental validation for solvents n-butyl acetate and toluene with COSMO-RS predictions (solid blue) vs. experimental data (dashed red) for T = 25 °C. Left: TZVP, Right: TZVPD-FINE, Top: n-butyl acetate, Bottom: toluene.

The results from experimental liquid-liquid measurements used in this work are given in Table 3 to Table 5.

Table 3: LLE Measurements for the system 2-methylfuran(2MF)-GVL-water with measurement uncertainties u at *T* = 25 °C and *T* = 40 °C.

T / °C	Phase	x_{2MF} / mol/mol	x_{GVL} / mol/mol	x_{WATER} / mol/mol	u(x_{2MF})	u(x_{GVL})	u(x_{WATER})
25	Organic	0.77260	0.21355	0.01385	0.02867	0.00486	0.00259
		0.50915	0.44014	0.05071	0.03421	0.01410	0.00707
		0.27455	0.48941	0.23604	0.00982	0.00787	0.01018
		0.13597	0.45028	0.41376	0.00998	0.01284	0.02810
		0.09880	0.42575	0.47545	0.00465	0.00751	0.01713
	Water	0.00120	0.01210	0.98670	0.00009	0.00054	0.00055
		0.00141	0.02108	0.97751	0.00010	0.00220	0.00215
		0.00174	0.03621	0.96205	0.00007	0.00164	0.00158
		0.00253	0.04641	0.95106	0.00004	0.00269	0.00256
		0.00319	0.05222	0.94459	0.00029	0.00286	0.00271
40	Organic	0.74571	0.24152	0.01277	0.01459	0.00360	0.00303
		0.45824	0.47047	0.07128	0.00961	0.00754	0.00894
		0.22304	0.45244	0.32452	0.00670	0.00723	0.01149
		0.10539	0.37558	0.51903	0.00826	0.01336	0.03381
	Water	0.00146	0.01008	0.98846	0.00011	0.00061	0.00061
		0.00173	0.02005	0.97822	0.00009	0.00125	0.00122
		0.00238	0.02944	0.96818	0.00011	0.00139	0.00135
		0.00332	0.03482	0.96186	0.00005	0.00197	0.00189

Table 4: LLE Measurements for the system toluene(TOL)-GVL-water with measurement uncertainties u at T = 25 °C and T = 40 °C.

T / °C	Phase	x_{TOL} / mol/mol	x_{GVL} / mol/mol	x_{WATER} / mol/mol	u(x_{2TOL})	u(x_{GVL})	u(x_{WATER})
25	Organic	0.80569	0.18196	0.01235	0.01009	0.01273	0.00023
		0.64384	0.30627	0.04989	0.00774	0.01256	0.00083
		0.36174	0.46608	0.17218	0.00389	0.01170	0.00269
		0.23200	0.50632	0.26168	0.00254	0.01220	0.00311
		0.17887	0.49810	0.32303	0.00145	0.00879	0.00333
		0.91565	0.08085	0.00350	0.01287	0.01410	0.00011
		0.88371	0.11169	0.00460	0.01229	0.01381	0.00226
		0.83528	0.15471	0.01001	0.01072	0.01299	0.00024
	Water	0.00199	0.02230	0.97570	0.00143	0.00089	0.00164
		0.00118	0.03876	0.96005	0.00058	0.00081	0.00096
		0.00220	0.04998	0.94781	0.00062	0.00101	0.00112
		0.00181	0.06064	0.93754	0.00005	0.00177	0.00166
		0.00244	0.07091	0.92665	0.00021	0.00131	0.00122
		0.00169	0.00281	0.99551	0.00242	0.00028	0.00242
		0.00125	0.01574	0.98302	0.00082	0.00438	0.00438
		0.00056	0.01743	0.98202	0.00018	0.00058	0.00060
40	Organic	0.82014	0.16417	0.01569	0.01180	0.01454	0.00114
		0.64324	0.29089	0.06587	0.00745	0.01196	0.00175
		0.36013	0.43588	0.20398	0.00698	0.01978	0.00848
		0.22163	0.47274	0.30563	0.00344	0.01617	0.00751
		0.17329	0.46342	0.36329	0.00251	0.01536	0.00689

		0.90145	0.08360	0.01495	0.01215	0.01361	0.00230
		0.84803	0.13114	0.02083	0.01137	0.01322	0.00210
		0.77588	0.20757	0.01655	0.01217	0.01439	0.00441
	Water	0.00084	0.02076	0.97840	0.00050	0.00062	0.00078
		0.00090	0.03314	0.96596	0.00023	0.00093	0.00093
		0.00181	0.04610	0.95209	0.00008	0.00185	0.00176
		0.00269	0.05982	0.93749	0.00014	0.00128	0.00120
		0.00309	0.06965	0.92726	0.00016	0.00321	0.00298
		0.00127	0.00359	0.99514	0.00033	0.00002	0.00033
		0.00119	0.01725	0.98156	0.00021	0.00033	0.00039
		0.00053	0.02194	0.97753	0.00009	0.00048	0.00048

Table 5: LLE Measurements for the system n-butyl acetate(nBAC)-GVL-water with measurement uncertainties u at T = 25 °C and T = 40 °C.

T / °C	Phase	x_{nBAC} / mol/mol	x_{GVL} / mol/mol	x_{WATER} / mol/mol	u(x_{nBAC})	u(x_{GVL})	u(x_{WATER})
25	Organic	0.61559	0.17204	0.21238	0.01141	0.01814	0.00631
		0.49997	0.28895	0.21108	0.01301	0.02673	0.00701
		0.36119	0.41873	0.22008	0.00665	0.01961	0.00551
		0.22874	0.50671	0.26456	0.00512	0.02478	0.00714
		0.09713	0.49307	0.40980	0.00223	0.02480	0.01141
	Water	0.00129	0.01909	0.97961	0.00009	0.00045	0.00045
		0.00140	0.02896	0.96964	0.00002	0.00103	0.00100
		0.00202	0.03485	0.96313	0.00007	0.00212	0.00204
		0.00288	0.04399	0.95313	0.00008	0.00168	0.00160
		0.00523	0.06494	0.92983	0.00009	0.00155	0.00144
40	Organic	0.61339	0.18763	0.19898	0.01350	0.02204	0.00589
		0.48482	0.29811	0.21707	0.01531	0.03257	0.00847
		0.36444	0.38247	0.25310	0.00978	0.02829	0.00842
		0.22653	0.47608	0.29738	0.00451	0.02160	0.00747
		0.08731	0.46160	0.45109	0.00308	0.03728	0.01935
	Water	0.00120	0.01815	0.98065	0.00005	0.00072	0.00071
		0.00145	0.02795	0.97061	0.00004	0.00099	0.00096
		0.00177	0.03774	0.96050	0.00003	0.00158	0.00151
		0.00307	0.04359	0.95334	0.00008	0.00252	0.00240
		0.00580	0.06588	0.92832	0.00015	0.00361	0.00335

3. Correlation coefficients

The Spearman's or Pearson correlation coefficient ρ determines if a correlation between two properties x and y is monotonous for a set of N sample values with mean values of $\bar{x}$ and $\bar{y}$. For $\rho = 1$, the relation is strictly monotonously increasing, i.e. $x_2 < x_1 \rightarrow y_2 < y_1$, and for $\rho = -1$ strictly monotonously decreasing. For $\rho \sim 0$ no monotony is found. For Spearman correlation, x and y denote rank indexes, whereas for Pearson correlation x and y can be any set of sample values.

$$\rho_{x,y} = \frac{\sum_{i=1}^{N}(x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum_{i=1}^{N}(x_i - \bar{x})^2}\sqrt{\sum_{i=1}^{N}(y_i - \bar{y})^2}}$$

4. Fragment library used in LEA3D optimization

Figure 2 shows the molecular fragments for the genetic algorithm LEA3D that are included in the initial molecular fragment libraries. The X marks a connector in the molecular fragment. Each X can be connected to an X from another molecular fragment in the genetic algorithm to build a new molecular structure. Unconnected connectors X are automatically replaced by hydrogen atoms. The structural feasibility of the molecular structures is ensured by LEA3D.

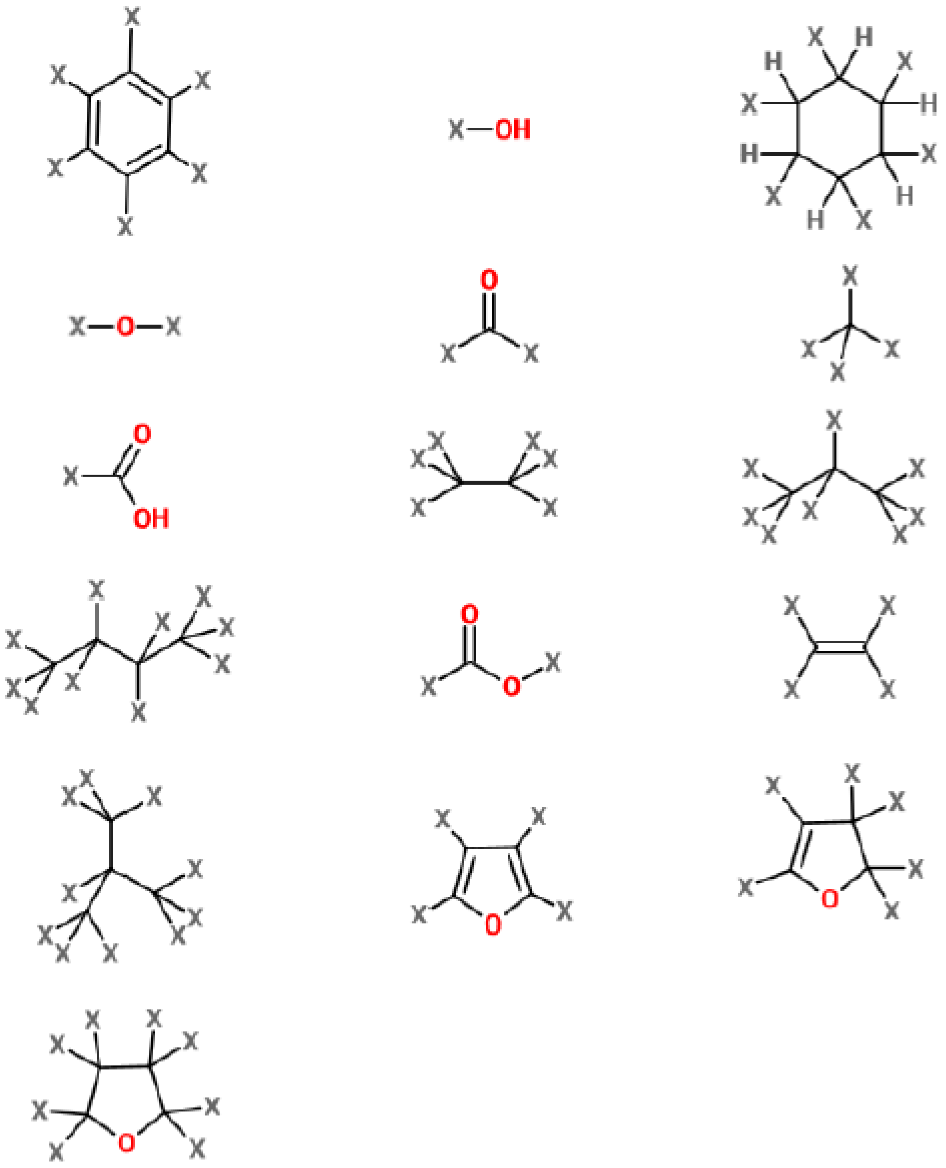

Figure 2: Molecular fragments used in LEA3D for COSMO-CAMPD optimization

5. Details on COSMO-CAMPD optimization

In this work, 3 consecutive COSMO-CAMPD optimization runs have been performed using 8 parallelized cores on an Intel Xeon CPU E5-1660v3@3.00GHz workstation. Table 6 shows statistics for all optimization runs. It should be emphasized that the time demand strongly correlates with the number of COSMOconf calculations.

Table 6: Statistics for the COSMO-CAMPD optimization for GVL. If a COSMO file is available, it is taken from the database, otherwise it is created by COSMOconf. Molecules that do not satisfy constraints, e.g., molecules exceeding specified molecular size, are not built.

	Run # 1	Run # 2	Run # 3
COSMOconf	237	70	152
Database	1,502	1,817	1,636
Not built	301	153	152
Time (d:h:m:s)	1:17:19:17	0:14:40:10	1:07:02:05

6. Process specifications for pinch-based process models

General process specifications are taken from Scheffczyk et al. 2016, the temperature of the extraction column is considered as a degree of freedom. Table 7 summarizes the most important process specifications.

Table 7: Process specifications for the hybrid extraction-distillation process

Unit operation	Extraction	Raffinate is free of GVL, Temperatur T_{extr} is optimized with respect to process minimum energy demand
	Distillation	GVL in the feed is recovered as pure stream at the bottom (sharp split). All entering and leaving streams are liquid and at 1 bar.
	Decanter	$T = 25$ °C.
Process Stream	Feed (F)	Composition is set to 0.95 mol/mol water, 0.05 mol/mol GVL

7. Rigorous validation of the screening results

Rigorous process model calculations using ASPEN Plus V8.4 are performed to validate the results from shortcut process models for the top solvents. The minimum energy demand Q_{min} is calculated by ASPEN Plus using the model “Radfrac”. A parametric study is performed to determine the minimum required energy demand to achieve 99.9% purity and recovery of the solute A in the bottom stream B. Infinite numbers of stages, that are assumed in the process shortcut, are approximated by using n = 50 stages (Feed stage at n = 25) in the distillation column.

References

D. Dechambre, C. Pauls, L. Greiner, K. Leonhard and A. Bardow, Towards automated characterisation of liquid–liquid equilibria, Fluid Phase Equilibria, 2014, 362, 328–334.

J. Scheffczyk, C. Redepenning, C. M. Jens, B. Winter, K. Leonhard, W. Marquardt,A. Bardow, Massive, automated solvent screening for minimum energy demand in hybrid extraction–distillation using COSMO-RS, Chemical Engineering Research and Design, 2016, 115, 433–442