processes

Supplementary Materials: Solubility Temperature Dependence of Bio-Based Levulinic Acid, Furfural and Hydroxymethylfurfural in Water, Nonpolar, Polar Aprotic and Protic Solvents

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Abbreviations:

FF	Furfural
LA	Levulinic acid
HMF	Hydroxymethylfurfural
DMSO	Dimethyl sulfoxide

The units for all below tables:

A (/); B (L g–1); c (g L–1); Solubility (g L–1)

The protocol for the assessment of solubility was as follows:

1.) Into 4 separate 5 mL vials 60, 150, 300, in 600 mg of the appropriate solute was weighed.
2.) To this solute 3 mL of the appropriate solvent was added (a calibrated 5 mL pipet was used).
3.) The solution was left to rest for 30 min, so that the solute completely dissolved.
4.) The FTIR probe was submerged in pure solvent and the background was equilibrated for 3 min.
5.) The probe was cleaned thoroughly and submerged into the vial with the lowest amount of added solute.
6.) After the FTIR signal was stable, the probe was removed, cleaned again and submerged into the next vial with the higher amount of solute.
7.) This was done for all solutes in all solvents, at all temperatures (where the solvent was liquid).
8.) From some vials 100 μL of the solution was taken and diluted (10-times) in 900 μL of the appropriate solvent.
9.) The diluted solution prepared in the previous line was analyzed with GC/MS to validate the check the actual concentration of solute.

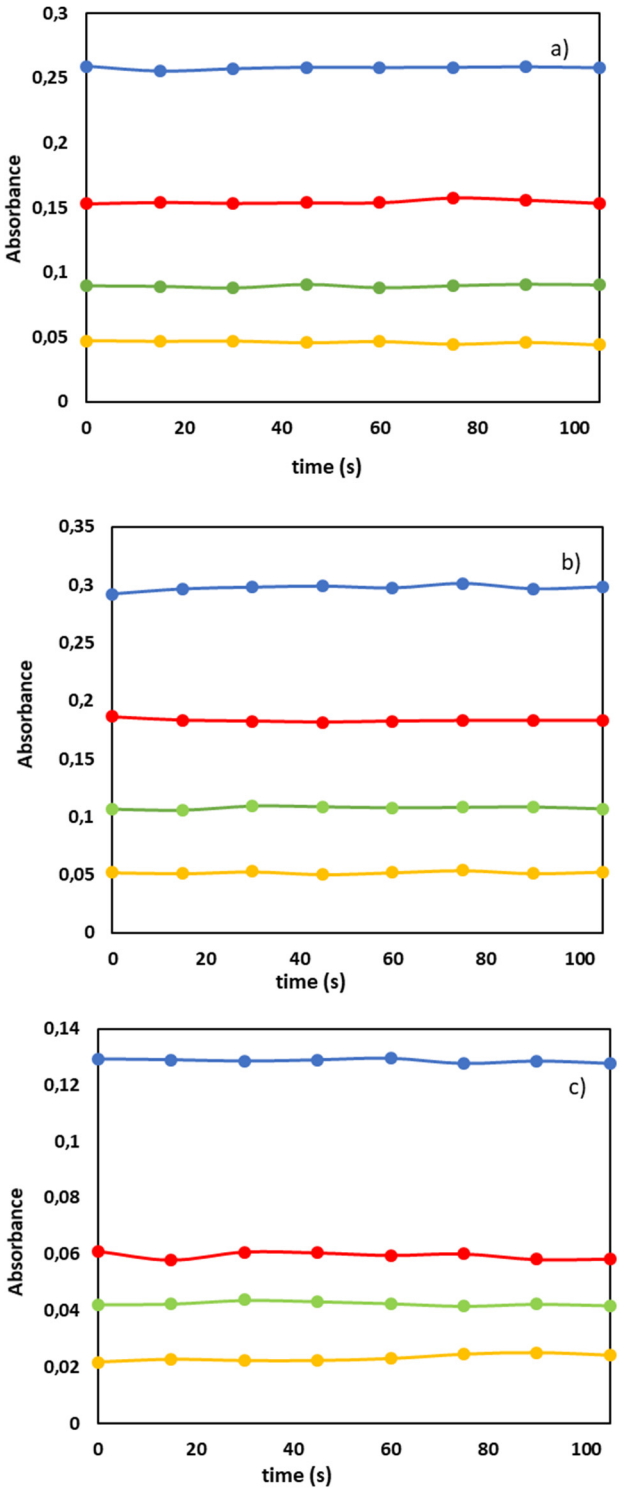

Figure S1. Dependence of the signal intensity versus time for furfural (a), levulinic acid (b) and HMF (c) in methanol at 25 °C, –20 g L^{-1}, –50 g L^{-1}, –100 g L^{-1}, –200 g L^{-1}.

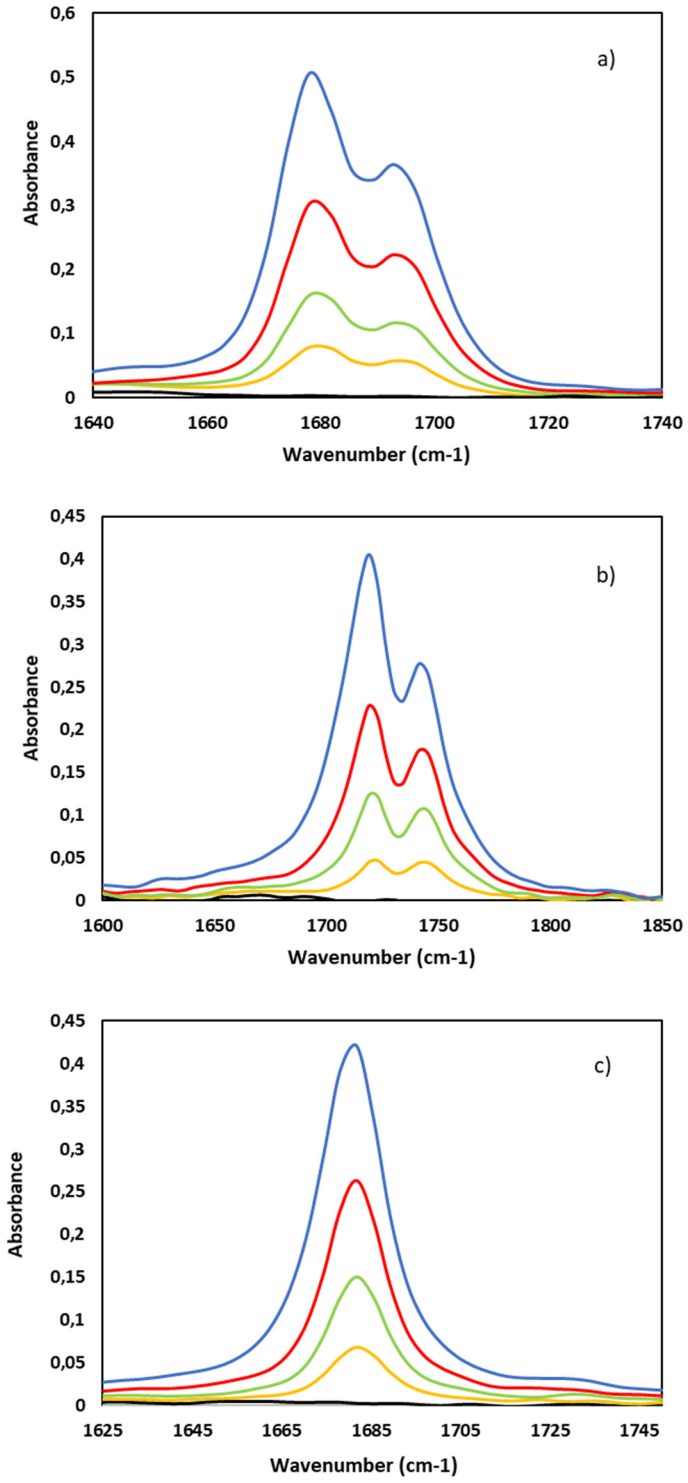

Figure S2. Absorbance of furfural (a), levulinic acid (b) and HMF (c) in acetonitrile at 25 °C; **–** (acetonitrile), –20 g L^{-1}, –50 g L^{-1}, –100 g L^{-1}, –200 g L^{-1}.

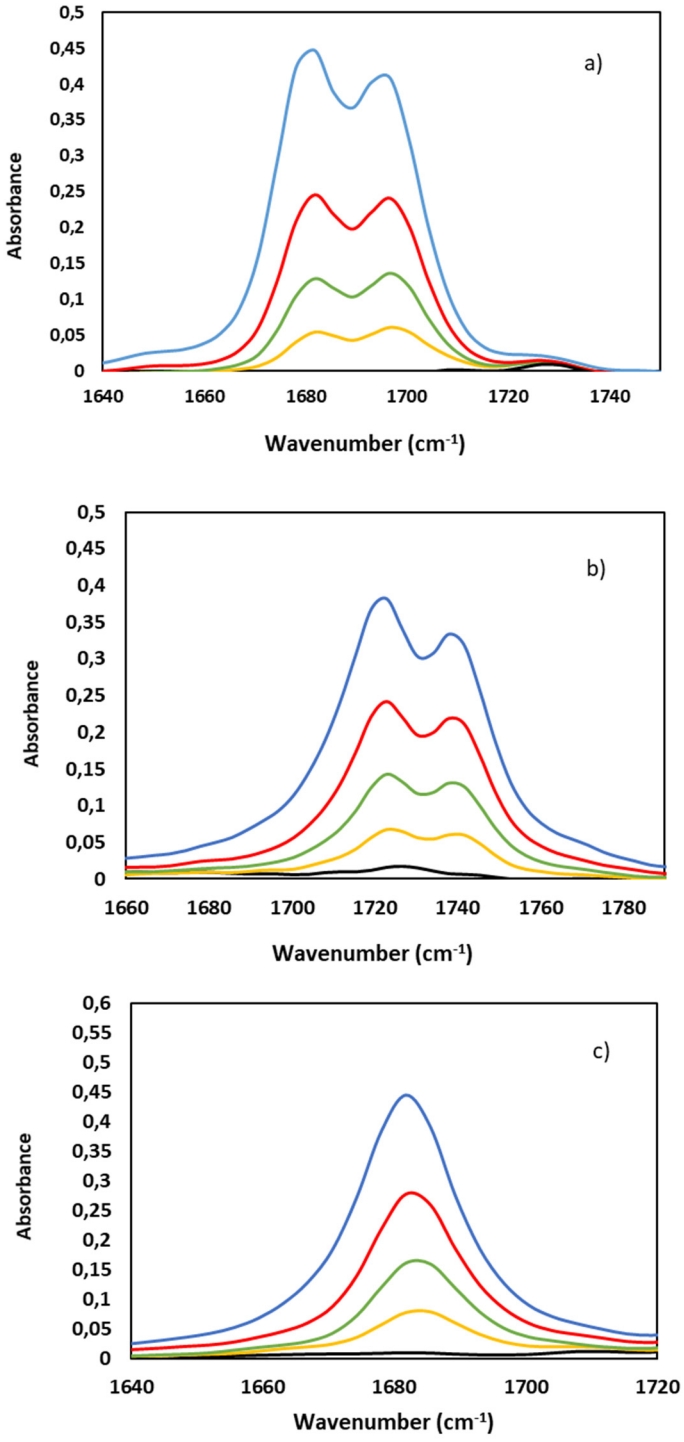

Figure S3. Absorbance of furfural (a), levulinic acid (b) and HMF (c) in 1,4-dioxane at 25 °C; – (1,4-dioxane), –20 g L^{-1}, –50 g L^{-1}, –100 g L^{-1}, –200 g L^{-1}.

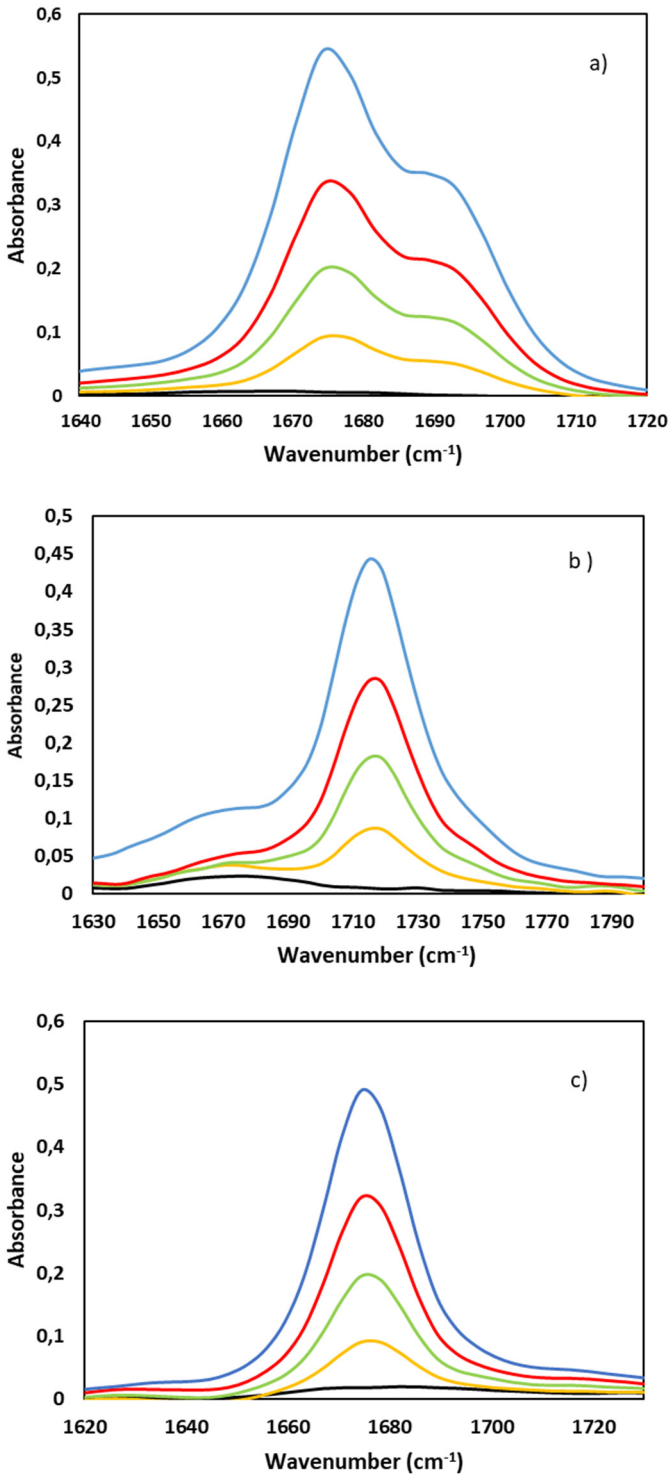

Figure S4. Absorbance of furfural (a), levulinic acid (b) and HMF (c) in DMSO at 25 °C; – (DMSO), –20 g L^{-1}, –50 g L^{-1}, –100 g L^{-1}, –200 g L^{-1}.

Table S1. The table contains some basic information for the three examined compounds and the selected solvents.

	Molecular Formula	Molecular Mass (g mol^{-1})	C	H	O	N	Cl	S	Polarity Index [1]	Dipole Moment (D)	DielecTric Constant
Levulinic acid	$C_5H_8O_3$	116.11	5	8	3	/	/	/		6.1	19.1
Furfural	$C_5H_4O_2$	96.08	5	4	2	/	/	/	0.4	8.3	41.8
Hydroxymethylfurfural	$C_6H_6O_3$	126.11	6	6	3	/	/	/		5.0	
n-Hexane	C_6H_{14}	86.18	6	14	/	/	/	/	0.1	0.0	2.0
Cyclohexane	C_6H_{12}	84.16	6	12	/	/	/	/	0.2	0.0	2.0
Benzene	C_6H_6	78.11	6	6	/	/	/	/	2.7	0.0	2.3
Toluene	C_6H_6–CH_3	92.14	6	9	/	/	/	/	2.4	0.4	2.4
1,4-dioxane	$C_4H_8O_2$	88.11	4	8	2	/	/	/	4.8	0.5	2.3
Chloroform	$CHCl_3$	119.38	1	/	/	/	3	/	4.8	1.0	4.8
Diethyl ether	$(C_2H_5)_2O_2$	74.12	4	10	2	/	/	/	2.8	1.2	4.3
Dichloromethane	CH_2Cl_2	84.93	1	2	/	/	2	/	3.1	1.6	9.1
THF	C_4H_8O	72.11	4	8	1	/	/	/	4.0	1.8	7.5
Ethyl acetate	$C_4H_8O_2$	88.11	4	8	2	/	/	/	4.4	1.8	6.0
Acetone	$(CH_3)_2CO$	58.08	3	6	1	/	/	/	5.1	2.9	20.7
Acetonitrile	CH_3CN	41.05	2	3	/	1	/	/	5.8	4.0	37.5
DMSO	$(CH_3)_2SO$	78.13	2	6	1	/	/	1	7.2	4.0	46.5
Formic acid	HCO_2H	46.03	1	2	2	/	/	/	6.0	1,4	58.0
n-Butanol	C_4H_9OH	74.12	4	10	1	/	/	/	3.9	1,4	58.0
n-Propanol	C_3H_8O	60.10	3	8	1	/	/	/	3.9	1.6	20.3
EtOH	C_2H_6O	46.07	2	6	1	/	/	/	5.2	1.7	24.3

MeOH	CH_3OH	32.04	1	4	1	/	/	/	5.1	1.7	32.6
Acetic acid	CH_3CO_2H	60.05	2	4	2	/	/	/	6.0	1.7	6.2
H_2O	H_2O	18.02	/	2	1	/	/	/	10.2	1.9	78.5

Table S2. Experimentally measured peak height at 1696 cm^{-1} for FF in different solvents at different temperatures.

Solvent	*c*	0	20	50	100	200
Acetone	25 °C	0.0000	0.0434	0.0986	0.1697	0.2686
	0 °C	0.0000	0.0372	0.1055	0.1757	0.2766
	–10 °C	0.0000	0.0608	0.1181	0.1886	0.3088
Acetonitrile[a]	25 °C	0.0009	0.0502	0.1104	0.1969	0.3223
	0 °C	0.0009	0.0576	0.1185	0.2039	0.3265
	–10 °C	0.0025	0.0546	0.1082	0.2042	0.3248
Dichloromethane	25 °C	−0.0102	0.0597	0.1432	0.2475	0.3961
	0 °C	0.0024	0.0698	0.1627	0.2611	0.4033
	–10 °C	−0.0086	0.0811	0.1822	0.2786	0.4153
Diethyl ether	25 °C	0.0019	0.0308	0.1091	0.2379	0.4044
	0 °C	0.0062	0.0525	0.1607	0.3180	0.4935
	–10 °C	0.0048	0.1015	0.3094	0.4922	0.6278
EtOAc	25 °C	0.0000	0.0466	0.1236	0.2085	0.3482
	0 °C	0.0000	0.0499	0.1322	0.2191	0.3533
	–10 °C	0.0000	0.0485	0.1283	0.2147	0.3431
EtOH	25 °C	0.0088	0.0455	0.0984	0.1697	0.2828
	0 °C	0.0036	0.0509	0.1070	0.1824	0.2946
	–10 °C	0.0085	0.0521	0.1091	0.1843	0.2913
H_2O	25 °C	0.0365	0.1981	0.2511	0.3000	/

[a]Total solubility was taken as the average of all three measurements.

Table S3. Experimentally measured peak height at 1696 cm^{-1} for FF in different solvents at different temperatures.

Solvent	*c*	0	20	50	100	200
MeOH	25 °C	0.0155	0.0461	0.0893	0.1542	0.2578
	0 °C	0.0236	0.0577	0.1032	0.1700	0.2729
	–10 °C	0.0200	0.0570	0.1050	0.1752	0.2753
n-Butanol	25 °C	0.0122	0.0544	0.1104	0.1923	0.3094
	0 °C	0.0136	0.0554	0.1168	0.2004	0.3191
	–10 °C	0.0155	0.0583	0.1207	0.2025	0.3214
n-Propanol	25 °C	0.0196	0.0570	0.1095	0.1839	0.3000
	0 °C	0.0193	0.0609	0.1136	0.1918	0.3123
	–10 °C	0.0224	0.0621	0.1164	0.1917	0.3058
THF	25 °C	−0.0142	0.0308	0.1091	0.2379	0.4044
	0 °C	0.0028	0.0731	0.1650	0.2828	0.4403
	–10 °C	0.0045	0.0860	0.1827	0.2734	0.4538
Toluene	25 °C	0.0229	0.0981	0.2049	0.3435	0.5114
	0 °C	0.0118	0.1075	0.2282	0.3643	0.5089
	–10 °C	0.0094	0.1160	0.2033	0.3231	0.4453
Benzene	25 °C	0.0009	0.0912	0.1986	0.3317	0.4936
DMSO	25 °C	0.0061	0.0914	0.2011	0.3344	0.5413
1,4-dioxane	25 °C	-0.0080	0.0591	0.1353	0.2413	0.4046

Table S4. Experimentally measured peak height at 1720 cm^{-1} for LA in different solvents at different temperatures.

Solvent	c	0	20	50	100	200
	25 °C	−0.0063	0.0345	0.0959	0.1822	0.3105
Acetone	0 °C	−0.0065	0.0382	0.1072	0.1989	0.4046
	–10 °C	−0.0111	0.0376	0.1066	0.2004	0.4192
	25 °C	−0.0004	0.0463	0.1245	0.2289	0.4050
Acetonitrile	0 °C	−0.0082	0.0424	0.1332	0.2446	0.4241
	–10 °C	0.0016	0.0528	0.1458	0.2675	0.4510
	25 °C	0.0000	0.0962	0.2063	0.3280	0.4887
Dichloromethane	0 °C	−0.0040	0.1178	0.2194	0.3486	0.5118
	–10 °C	0.0027	0.1241	0.2227	0.3486	0.5128
	25 °C	−0.0081	0.0948	0.2052	0.3214	0.4960
Diethyl ether	0 °C	−0.0005	0.0886	0.1985	0.3196	0.4826
	–10 °C	0.0143	0.0997	0.2077	0.3432	0.5188
	25 °C	0.0000	0.0600	0.1318	0.2249	0.3627
EtOAc	0 °C	0.0000	0.0616	0.1516	0.2356	0.3719
	–10 °C	0.0000	0.1216	0.1958	0.2830	0.4090
	25 °C	0.0075	0.0575	0.1178	0.1877	0.3216
EtOH	0 °C	0.0085	0.0580	0.1182	0.1845	0.2626
	–10 °C	0.0069	0.0567	0.1253	0.2053	0.3979

Table S5. Experimentally measured peak height at 1720 cm^{-1} for LA in different solvents at different temperatures.

Solvent	*c*	0	20	50	100	200
	25 °C	0.0155	0.0520	0.1078	0.1832	0.2976
MeOH	0 °C	0.0236	0.0510	0.1059	0.1846	0.3000
	–10 °C	0.0200	0.0541	0.1001	0.1871	0.3017
	25 °C	0.0101	0.0680	0.1377	0.2294	0.3685
n-Butanol	0 °C	0.0188	0.0697	0.1402	0.2334	0.3875
	–10 °C	0.0129	0.0609	0.1317	0.2253	0.3644
	25 °C	0.0126	0.0633	0.1368	0.2220	0.3612
n-Propanol	0 °C	0.0145	0.0564	0.1380	0.2629	0.3823
	–10 °C	0.0161	0.0653	0.1504	0.2565	0.3734
	25° C	0.0028	0.0466	0.1107	0.1984	0.3542
THF	0 °C	0.0020	0.0559	0.1352	0.2350	0.4068
	–10 °C	0.0008	0.0750	0.1570	0.2754	0.4518
	25 °C	0.0050	0.1223	0.2246	0.3365	0.4950
Toluene	0 °C	0.0024	0.1133	0.2363	0.3627	0.5065
	–10 °C	0.0074	0.1145	0.4956	0.5270	0.6592
Benzene	25 °C	−0.0255	0.1280	0.2408	0.3738	0.5196
DMSO	25 °C	0.0077	0.0866	0.1787	0.2800	0.4315
1,4-dioxane	25 °C	0.0092	0.0591	0.1353	0.2413	0.4046
H_2O	25 °C			*no data*		

Table S6. Experimentally measured peak height at 1673 cm^{-1} for HMF in different solvents at different temperatures.

Solvent	c	0	20	50	100	200
	25°C	0.0000	0.0317	0.0764	0.1441	0.2747
Acetone	0°C	0.0000	0.0368	0.0935	0.1669	0.3160
	–10°C	0.0000	0.0441	0.1026	0.1906	0.3430
	25°C	0.0038	0.0363	0.0800	0.1549	0.2923
Acetonitrile	0°C	0.0023	0.0151	0.0692	0.1534	0.3038
	–10°C	0.0016	0.0499	0.0994	0.1863	0.3328
	25°C	0.0207	0.0847	0.1591	0.2649	0.4171
Dichloromethane	0°C	0.0257	0.0885	0.1696	0.3004	0.4344
	–10°C	0.0274	0.0871	0.2146	0.3176	0.4813
	25°C					
Diethyl ether	0°C			*insoluble*		
	–10°C					
	25°C	0.0000	0.0691	0.1351	0.2341	0.3586
EtOAc	0°C	0.0000	0.0495	0.0737	0.1507	0.2824
	–10°C	0.0000	0.0425	0.0692	0.0953	0.1634
	25°C	0.0101	0.0542	0.1171	0.1867	0.3253
EtOH	0°C	0.0196	0.0650	0.1274	0.2026	0.3361
	–10°C	0.0010	0.0624	0.1224	0.1948	0.3082

Table S7. Experimentally measured peak height at 1673 cm^{-1} for HMF in different solvents at different temperatures.

Solvent	*c*	0	20	50	100	200
	25°C	0.0062	0.0232	0.0425	0.0596	0.1287
MeOH	0°C	0.0030	0.0535	0.1015	0.1753	0.2977
	–10°C	-0.0004	0.0293	0.0680	0.0985	0.1533
	25°C	0.0176	0.0502	0.1291	0.2199	0.3510
n-Butanol	0°C	0.0189	0.0525	0.1405	0.2317	0.3504
	–10°C	0.0115	0.0377	0.1070	0.2099	0.3390
	25°C	0.0238	0.0707	0.1340	0.2228	0.3529
n-Propanol	0°C	0.0330	0.0905	0.1579	0.2466	0.3700
	–10°C	0.0322	0.0897	0.1571	0.2624	0.3842
	25°C	0.0080	0.0237	0.0447	0.1015	0.2185
THF	0°C	0.0162	0.0412	0.0809	0.1397	0.2965
	–10°C	0.0208	0.0871	0.2146	0.3176	0.4813
	25°C					
Toluene	0°C			*insoluble*		
	–10°C					
Benzene	25°C			*insoluble*		
DMSO	25°C	0.0139	0.0901	0.1961	0.3195	0.4922
1,4-dioxane	25°C	0.0097	0.1662	0.3110	0.3904	0.4218
H_2O	25°C	0.0007	0.1662	0.3110	0.3904	0.4218

Table S8. The table contains the correlation factors (A and B from Eq. (1), in section 3.4 of the main text) and max solubility for FF at different temperatures and in different solvents.

Solvent	Temperature								
	–10 °C			0 °C			25 °C		
	A	B	Solubility	A	B	Solubility	A	B	Solubility
Benzene	/	/	/	/	/	/	0.637	0.008	566
Toluene	0.499	0.011	426	0.594	0.010	478	0.657	0.008	614
1,4-Dioxane	/	/	/	/	/	/	0.718	0.004	1113
Diethyl ether	0.717	0.011	423	0.848	0.004	1042	1.235	0.002	2302*
Dichloro-methane	0.506	0.008	547	0.537	0.007	669	0.606	0.005	871
THF	0.628	0.006	735	0.625	0.006	758	1.235	0.002	2302*
EtOAc	0.516	0.005	845	0.536	0.005	860	0.589	0.004	1032
Acetone	0.436	0.006	760	0.407	0.006	809	0.396	0.006	813
Acetonitrilea	0.516	0.005	926	0.482	0.006	820	0.529	0.005	982
DMSO	/	/	/	/	/	/	0.801	0.006	824
n-Butanol	0.455	0.006	759	0.467	0.006	805	0.466	0.005	848
n-Propanol	0.420	0.006	719	0.457	0.006	810	0.441	0.006	818
EtOH	0.413	0.006	760	0.441	0.005	839	0.465	0.005	989
MeOH	0.372	0.007	692	0.375	0.006	722	0.416	0.005	961

*Fully miscible. [a]Total solubility was taken as the average of all three measurements.

Table S9. Correlation factors and max solubility for LA at different temperatures and in different solvents.

Solvent	Temperature								
	–10 °C			0 °C			25 °C		
	A	B	Solubility	A	B	Solubility	A	B	Solubility
Benzene	/	/	/	/	/	/	0.585	0.011	433
Toluene	0.672	0.018	251	0.577	0.010	448	0.569	0.010	471
1,4-Dioxane	/	/	/	/	/	/	0.616	0.005	1017
Diethyl ether	0.672	0.007	629	0.620	0.007	617	0.639	0.007	624
Dichloro-methane	0.604	0.009	501	0.611	0.009	518	0.607	0.008	572
THF	0.722	0.005	942	0.786	0.004	1269*	0.821	0.003	1636*
EtOAc	0.444	0.012	397	0.503	0.007	694	0.547	0.005	851
Acetone	351.197	0.000	777810*	18.765	0.000	42361*	0.681	0.003	1507*
Acetonitrile	0.892	0.004	1304*	0.979	0.003	1618*	0.990	0.003	1751*
DMSO	/	/	/	/	/	/	0.550	0.008	611

n-Butanol	0.552	0.005	858	0.594	0.005	881	0.528	0.006	778
n-Propanol	0.479	0.008	608	0.536	0.006	725	0.524	0.006	798
EtOH	1.175	0.002	2245*	0.306	0.010	479	0.508	0.005	932
MeOH	0.481	0.005	936	0.465	0.005	893	0.447	0.005	848

*Fully miscible.

Table S10. Correlation factors and max solubility for HMF at different temperatures and in different solvents.

Solvent	Temperature								
	–10 °C			**0 °C**			**25 °C**		
	A	**B**	**Solubility**	**A**	**B**	**Solubility**	**A**	**B**	**Solubility**
1,4-Dioxane	/	/	/	/	/	/	2.242	0.001	7039*
Dichloro-methane	0.593	0.008	562	0.551	0.008	592	0.567	0.007	701
THF	0.593	0.008	563	70.683	0.000	220011*	263.337	0.000	1134229*
EtOAc	0.206	0.007	621	0.982	0.002	2725*	0.486	0.007	692
Acetone	0.892	0.002	1899*	1.120	0.002	2786*	1.270	0.001	3783*
Acetonitrile	0.755	0.003	1577*	36.775	0.000	111777*	1.237	0.001	3418*
DMSO	/	/	/	/	/	/	0.653	0.007	664
n-Butanol	0.639	0.004	1207	0.473	0.007	680	0.534	0.005	860
n-Propanol	0.468	0.008	543	0.441	0.009	523	0.485	0.006	716
EtOH	0.409	0.007	671	0.486	0.006	795	0.546	0.004	1030
MeOH	0.190	0.008	578	0.498	0.005	1020	0.466	0.002	2895*
H_2O	/	/	/	/	/	/	0.425	0.026	180

*Fully miscible.

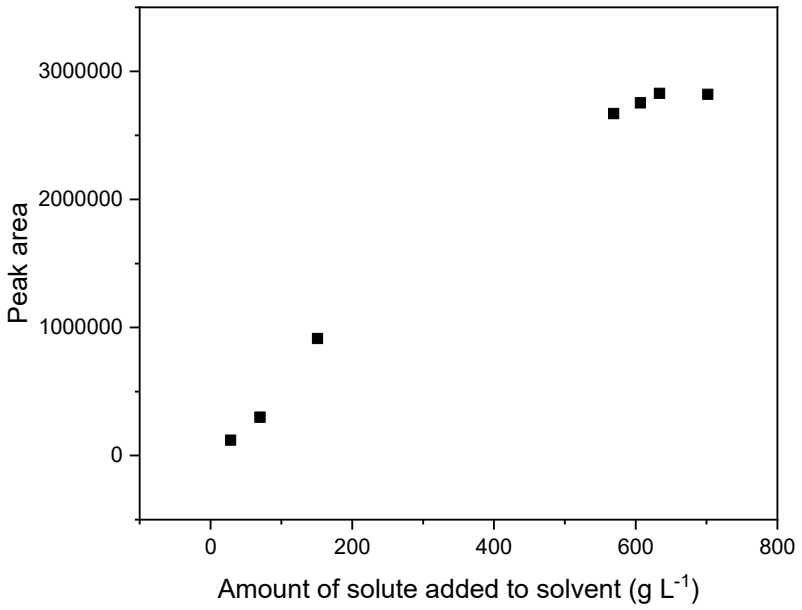

Figure S5. The validation experiment using GC/MS for furfural in benzene.

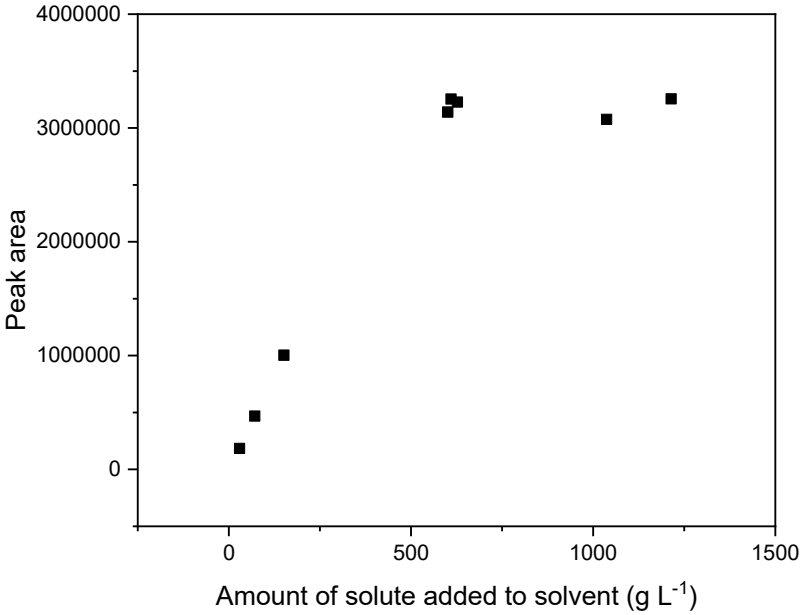

Figure S6. The validation experiment using GC/MS for levulinic acid in DMSO.

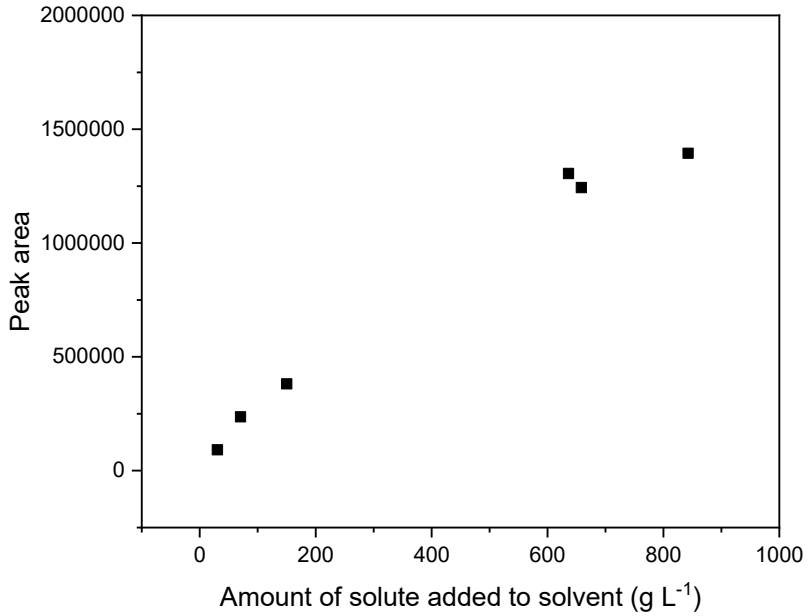

Figure S7. The validation experiment using GC/MS for HMF in EtOAc.

References

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