SUPPORTING INFORMATION

Quantitative Vibrational Spectroscopy on Liquid Mixtures:

Concentration Units Matter

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This Supporting Information contains the following:

- **Tables S1-S4:** Compositional details of the 4 binary solvent mixtures used in this study
- **Figures S1-S4:** Raw NIR, Raman, and MIR spectra of the 4 binary solvent mixtures used in this study
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- **Table S5:** PLS results (RMSEP values using 1 LV) of the 4 binary solvent mixtures for NIR, Raman, and MIR data, using both mass and volume fractions as concentration units.
- Procedure for PLS simulations
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Table S1: Compositional details of the formulated chloroform-heptane mixtures.

Sample number	Mass fraction chloroform	Mass fraction heptane	Volume fraction chloroform	Volume fraction heptane
Calibration samples				
1	1	0	1	0
2	0.9579	0.0421	0.9125	0.0875
3	0.9140	0.0860	0.8296	0.1704
4	0.8707	0.1293	0.7554	0.2446
5	0.8263	0.1737	0.6856	0.3144
6	0.7810	0.2190	0.6205	0.3795
7	0.7358	0.2642	0.5608	0.4392
8	0.6886	0.3114	0.5034	0.4966
9	0.6413	0.3587	0.4504	0.5496
10	0.5932	0.4068	0.4007	0.5993
11	0.5435	0.4565	0.3531	0.6469
12	0.4943	0.5057	0.3094	0.6906
13	0.4430	0.5570	0.2672	0.7328
14	0.3919	0.6081	0.2281	0.7719
15	0.3388	0.6612	0.1903	0.8097
16	0.2854	0.7146	0.1548	0.8452
17	0.2308	0.7692	0.1209	0.8791
18	0.1743	0.8257	0.0882	0.9118
19	0.1172	0.8828	0.0574	0.9426
20	0.0595	0.9405	0.0282	0.9718
21	0	1	0	1
Test samples				
1	0.9780	0.0220	0.9533	0.0467
2	0.8764	0.1236	0.7648	0.2352
3	0.7702	0.2298	0.6057	0.3943
4	0.6590	0.3410	0.4698	0.5302
5	0.5441	0.4559	0.3536	0.6464
6	0.4231	0.5769	0.2516	0.7484
7	0.2976	0.7024	0.1626	0.8374
8	0.1669	0.8331	0.0841	0.9159
9	0.0286	0.9714	0.0133	0.9867

Table S2: Compositional details of the formulated chloroform-toluene mixtures.

Sample number	Mass fraction chloroform	Mass fraction toluene	Volume fraction chloroform	Volume fraction toluene
Calibration samples				
1	1	0	1	0
2	0.9608	0.0392	0.9343	0.0657
3	0.9215	0.0785	0.8719	0.1281
4	0.8805	0.1195	0.8104	0.1896
5	0.8384	0.1616	0.7505	0.2495
6	0.7955	0.2045	0.6928	0.3072
7	0.7516	0.2484	0.6369	0.3631
8	0.7072	0.2928	0.5834	0.4166
9	0.6603	0.3397	0.5298	0.4702
10	0.6130	0.3870	0.4787	0.5213
11	0.5645	0.4355	0.4291	0.5709
12	0.5145	0.4855	0.3806	0.6194
13	0.4632	0.5368	0.3334	0.6666
14	0.4112	0.5888	0.2882	0.7118
15	0.3568	0.6432	0.2434	0.7566
16	0.3015	0.6985	0.2002	0.7998
17	0.2442	0.7558	0.1578	0.8422
18	0.1861	0.8139	0.1170	0.8830
19	0.1256	0.8744	0.0769	0.9231
20	0.0640	0.9360	0.0381	0.9619
21	0	1	0	1
Test samples				
1	0.9806	0.0194	0.9669	0.0331
2	0.8854	0.1146	0.8175	0.1825
3	0.7846	0.2154	0.6787	0.3213
4	0.6777	0.3223	0.5493	0.4507
5	0.5645	0.4355	0.4291	0.5709
6	0.4438	0.5562	0.3163	0.6837
7	0.3163	0.6837	0.2115	0.7885
8	0.1793	0.8207	0.1124	0.8876
9	0.0313	0.9687	0.0184	0.9816

Table S3: Compositional details of the formulated toluene-heptane mixtures.

Sample number	Mass fraction toluene	Mass fraction heptane	Volume fraction toluene	Volume fraction heptane
Calibration samples				
1	1	0	1	0
2	0.9450	0.0550	0.9314	0.0686
3	0.8915	0.1085	0.8666	0.1334
4	0.8382	0.1618	0.8038	0.1962
5	0.7861	0.2139	0.7439	0.2561
6	0.7337	0.2663	0.6854	0.3146
7	0.6821	0.3179	0.6292	0.3708
8	0.6301	0.3699	0.5740	0.4260
9	0.5793	0.4207	0.5213	0.4787
10	0.5294	0.4706	0.4708	0.5292
11	0.4792	0.5208	0.4212	0.5788
12	0.4291	0.5709	0.3727	0.6273
13	0.3806	0.6194	0.3270	0.6730
14	0.3312	0.6688	0.2814	0.7186
15	0.2823	0.7177	0.2372	0.7628
16	0.2353	0.7647	0.1957	0.8043
17	0.1874	0.8126	0.1542	0.8458
18	0.1399	0.8601	0.1139	0.8861
19	0.0941	0.9059	0.0759	0.9241
20	0.0473	0.9527	0.0378	0.9622
21	0	1	0	1
Test samples				
1	0.9728	0.0272	0.9658	0.0342
2	0.8450	0.1550	0.8117	0.1883
3	0.7211	0.2789	0.6715	0.3285
4	0.5986	0.4014	0.5411	0.4589
5	0.4790	0.5210	0.4210	0.5790
6	0.3618	0.6382	0.3096	0.6904
7	0.2467	0.7533	0.2057	0.7943
8	0.1337	0.8663	0.1087	0.8913
9	0.0232	0.9768	0.0184	0.9816

Table S4: Compositional details of the formulated MEK-heptane mixtures.

Sample number	Mass fraction MEK	Mass fraction heptane	Volume fraction MEK	Volume fraction heptane
Calibration samples				
1	1	0	1	0
2	0.9323	0.0677	0.9212	0.0788
3	0.8662	0.1338	0.8462	0.1538
4	0.8028	0.1972	0.7757	0.2243
5	0.7419	0.2581	0.7095	0.2905
6	0.6835	0.3165	0.6472	0.3528
7	0.6267	0.3733	0.5879	0.4121
8	0.5713	0.4287	0.5310	0.4690
9	0.5191	0.4809	0.4784	0.5216
10	0.4675	0.5325	0.4272	0.5728
11	0.4185	0.5815	0.3795	0.6205
12	0.3699	0.6301	0.3328	0.6672
13	0.3239	0.6761	0.2893	0.7107
14	0.2801	0.7199	0.2485	0.7515
15	0.2353	0.7647	0.2073	0.7927
16	0.1937	0.8063	0.1695	0.8305
17	0.1530	0.8470	0.1330	0.8670
18	0.1134	0.8866	0.0980	0.9020
19	0.0739	0.9261	0.0635	0.9365
20	0.0377	0.9623	0.0322	0.9678
21	0	1	0	1
Test samples				
1	0.9657	0.0343	0.9599	0.0401
2	0.8109	0.1891	0.7847	0.2153
3	0.6697	0.3303	0.6327	0.3673
4	0.5387	0.4613	0.4981	0.5019
5	0.4184	0.5816	0.3794	0.6206
6	0.3069	0.6931	0.2734	0.7266
7	0.2040	0.7960	0.1788	0.8212
8	0.1081	0.8919	0.0933	0.9067
9	0.0173	0.9827	0.0148	0.9852

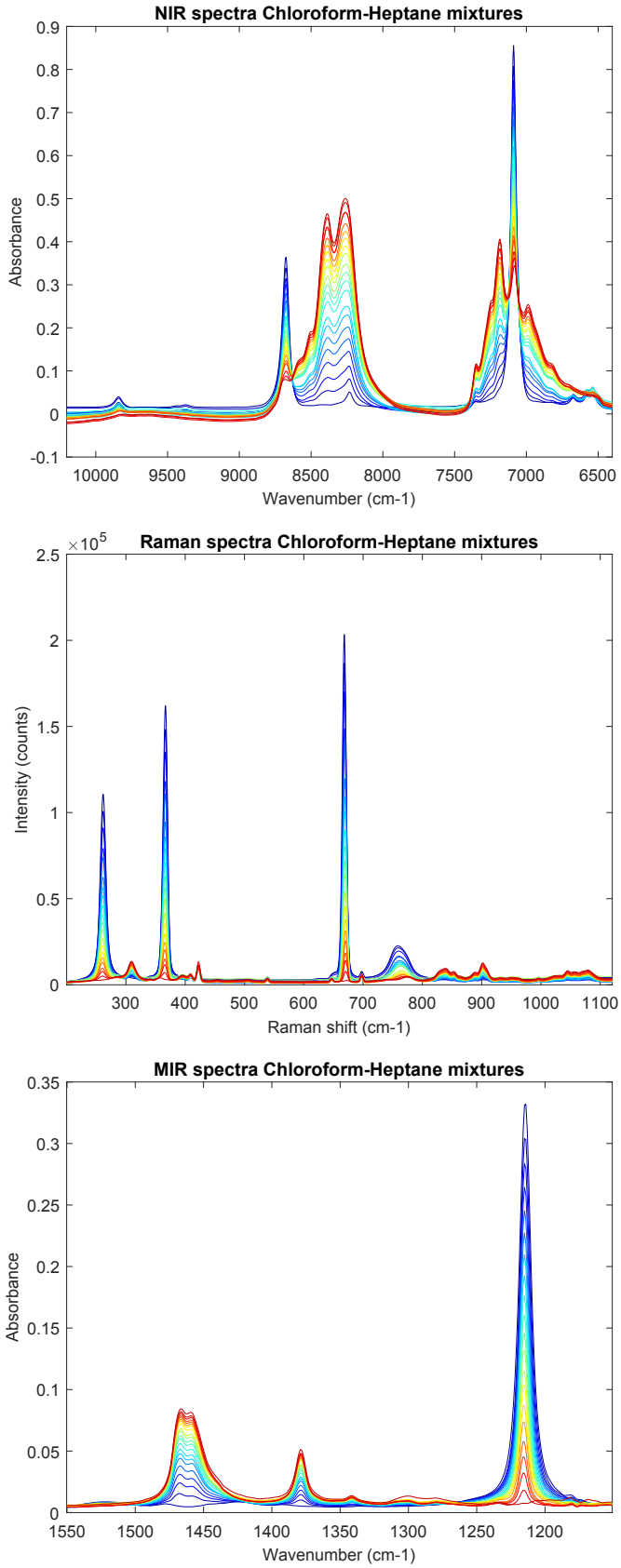

Figure S1. Raw NIR, Raman, and MIR spectra of chloroform-heptane mixtures; color map ranging from pure chloroform (blue) to pure heptane (red).

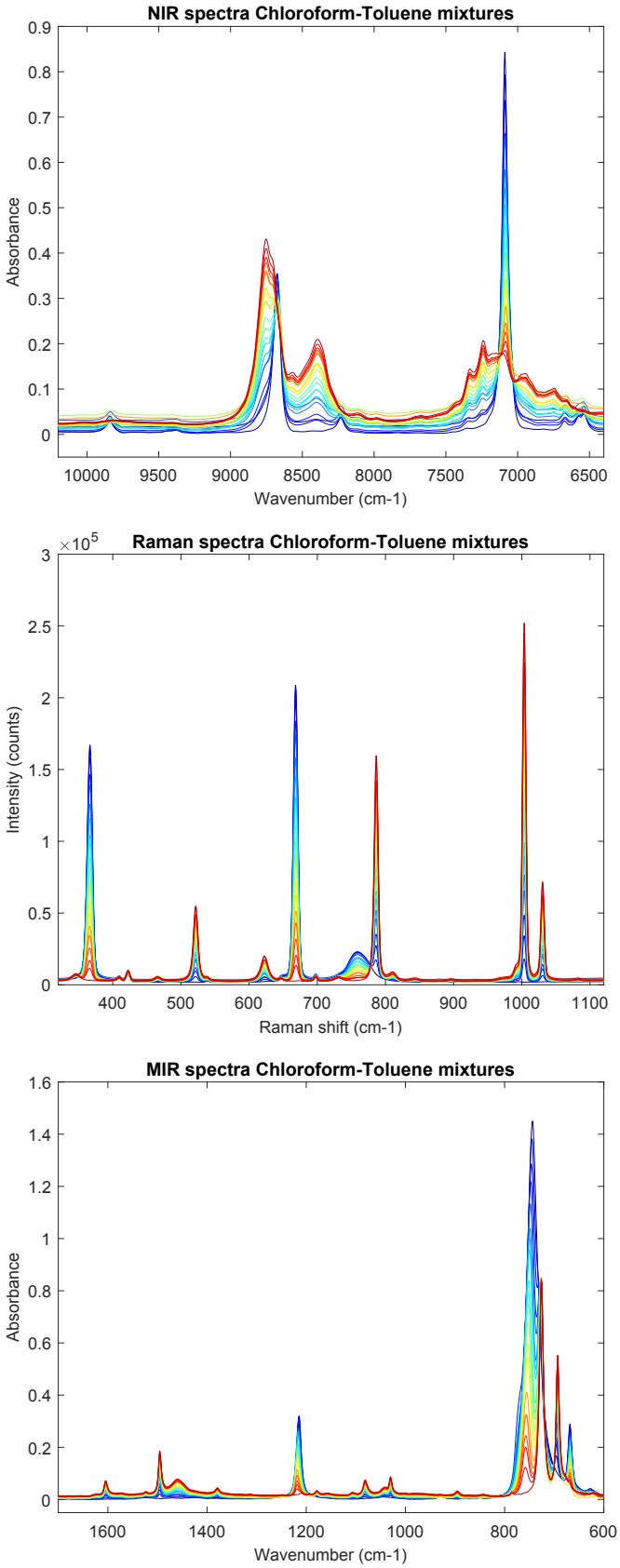

Figure S2. Raw NIR, Raman, and MIR spectra of chloroform-toluene mixtures; color map ranging from pure chloroform (blue) to pure toluene (red).

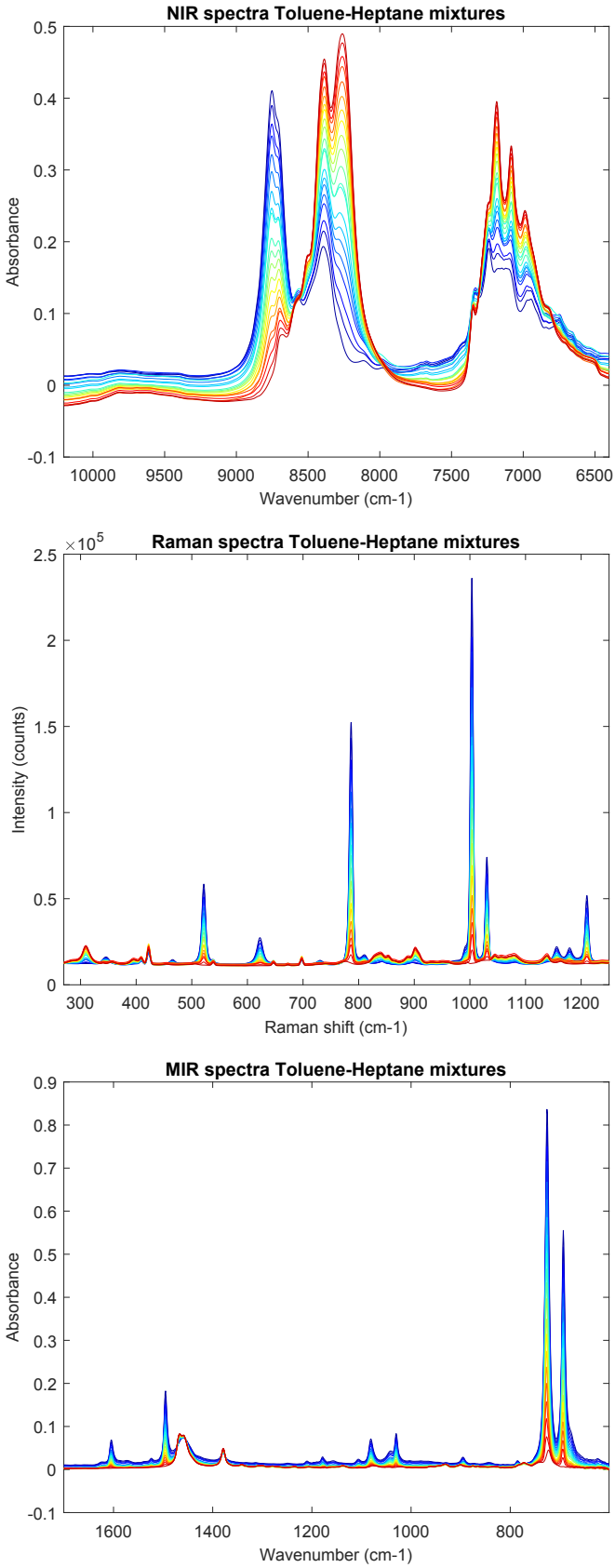

Figure S3. Raw NIR, Raman, and MIR spectra of Toluene-Heptane mixtures; color map ranging from pure toluene (blue) to pure heptane (red).

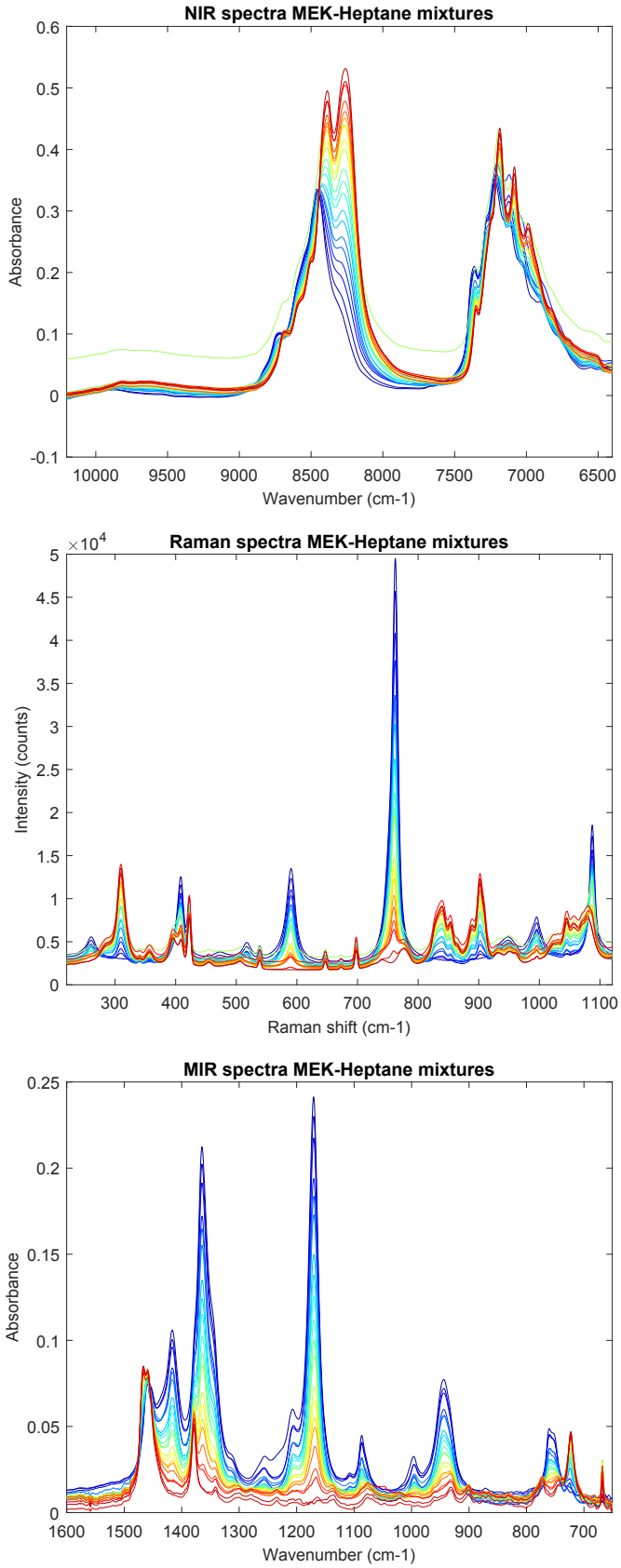

Figure S4. Raw NIR, Raman, and MIR spectra of MEK-Heptane mixtures; color map ranging from pure MEK (blue) to pure heptane (red).

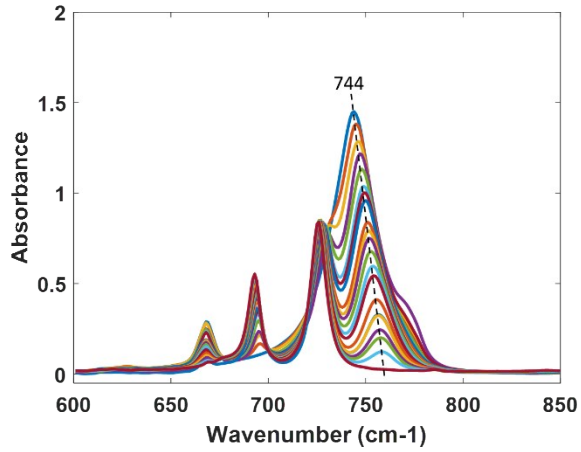

Figure S5. MIR spectra of the chloroform-toluene mixture. The antisymmetric CCl_3 band of chloroform gradually shifts from 744 to 758 cm^{-1} upon mixing with toluene.

Table S5: PLS results (RMSEP values using 1 LV) of the 4 binary solvent mixtures for NIR, Raman, and MIR data, using both mass and volume fractions as concentration units.

Binary system	Component	RMSEP values for NIR		RMSEP values for Raman		RMSEP values for MIR	
		Mass fraction	Volume fraction	Mass fraction	Volume fraction	Mass fraction	Volume fraction
Chloroform-Heptane mixtures	Chloroform	0.049	0.016	0.075	0.015	0.036	0.034
Chloroform-Toluene mixtures	Chloroform	0.066	0.023	0.050	0.010	0.048	0.024
Toluene-Heptane mixtures	Toluene	0.012	0.008	0.027	0.040	0.020	0.039
MEK-Heptane mixtures	MEK	0.005	0.018	0.022	0.017	0.027	0.020s

PLS simulations

For 15 hypothetical binary solvent systems with widely varying density differences (see Table S1), 21 mixture spectra per system were simulated as single noise-free Gaussian peaks (without peak shifts) scaling in intensity with volume fraction. This was done for the mass fraction ranges 0–1, 0–0.1, and 0–0.01, producing 45 data sets in total. An example of a data set simulated in this way is shown in Figure S2. PLS regression was applied to all of these data sets, using mass fractions as reference data. RMSECV values were calculated using 7-fold Venetian blinds cross-validation. The RMSECV values, expressed as relative numbers to the mean of the relevant mass fraction range, are plotted in Figure 6 of the article.

Table S6. Hypothetical binary liquid systems used for PLS simulations.

System	Component 1 Density (kg L^{-1})	Component 2 Density (kg L^{-1})	$\Delta\rho$ (kg L^{-1})
1	Tetrachloromethane 1.5940	Dichloromethane 1.3266	0.2674
2	Tetrachloromethane 1.5940	Ethylene glycol 1.1088	0.4852
3	Tetrachloromethane 1.5940	Ethyl acetate 0.9003	0.6937
4	Tetrachloromethane 1.5940	n-Heptane 0.6837	0.9103
5	Tetrachloromethane 1.5940	n-Pentane 0.6262	0.9678
6	Dichloromethane 1.3266	Ethylene glycol 1.1088	0.2178
7	Dichloromethane 1.3266	Ethyl acetate 0.9003	0.4263
8	Dichloromethane 1.3266	n-Heptane 0.6837	0.6429
9	Dichloromethane 1.3266	n-Pentane 0.6262	0.7004
10	Ethylene glycol 1.1088	Ethyl acetate 0.9003	0.2085
11	Ethylene glycol 1.1088	n-Heptane 0.6837	0.4251
12	Ethylene glycol 1.1088	n-Pentane 0.6262	0.4826
13	Ethyl acetate 0.9003	n-Heptane 0.6837	0.2166
14	Ethyl acetate 0.9003	n-Pentane 0.6262	0.2741
15	n-Heptane 0.6837	n-Pentane 0.6262	0.0575

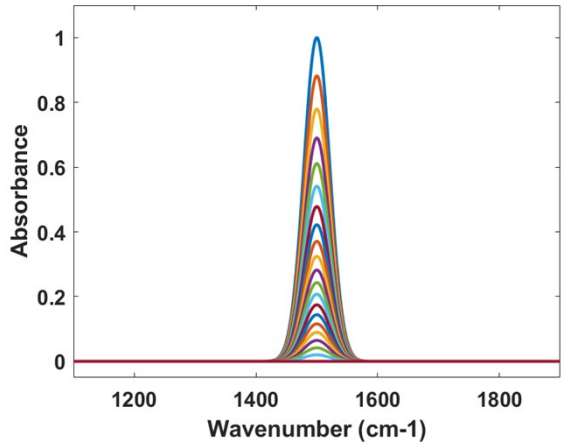

Figure S6. Simulated spectra of the tetrachloromethane-pentane mixture in the mass fraction range 0–1.