Supplementary Materials

Thermodynamic Surface Characterization of Sustainable Polymers by Advanced Inverse Gas Chromatography Revealing Nonlinear Lewis Acid–Base Interactions for Environmental and Biomedical Applications

Tayssir Hamieh [a,b,c*],

[a] Faculty of Science and Engineering, Maastricht University, P.O. Box 616, 6200 MD Maastricht, The Netherlands, Email: t.hamieh@maastrichtuniversity.nl

[b] Institut de Science des Matériaux de Mulhouse, Université de Haute-Alsace, CNRS, IS2M UMR 7361, F-68100 Mulhouse, France

[c] Laboratory of Materials, Catalysis, Environment and Analytical Methods Laboratory (MCEMA), and LEDDAR Laboratory, Lebanese University, Hadath, Lebanon.

[*] Correspondence: t.hamieh@maastrichtuniversity.nl.

Table S1. Variations of London dispersive free energy $\Delta G_a^d(T)$ (in kJ/mol) of PLA and CA as a function of temperature.

	PLA							
Solvents	303.15	308.15	313.15	318.15	323.15	328.15	333.15	338.15
n-Pentane	17.936	18.121	18.326	18.467	18.607	18.835	19.043	19.228
n-Hexane	22.972	23.104	23.229	23.383	23.536	23.646	23.761	23.893
n-Heptane	28.124	28.232	28.350	28.454	28.558	28.670	28.772	28.880
n-Octane	32.846	32.956	33.067	33.182	33.297	33.402	33.506	33.616
n-Nonane	37.223	37.331	37.440	37.540	37.639	37.754	37.868	37.976
CCl4	18.843	18.992	19.154	19.286	19.426	19.583	19.736	19.885

Nitromethane	16.984	17.171	17.377	17.537	17.701	17.911	18.108	18.295
CH2 Cl2	16.943	17.132	17.339	17.499	17.664	17.875	18.072	18.261
Chloroform	17.800	17.971	18.158	18.305	18.458	18.645	18.823	18.993
Diethyl ether	17.667	17.840	18.031	18.180	18.335	18.526	18.706	18.880
THF	17.056	17.241	17.446	17.604	17.768	17.976	18.171	18.357
Ethyl acetate	17.645	17.819	18.010	18.159	18.315	18.506	18.687	18.861
Acetone	16.256	16.459	16.682	16.852	17.027	17.257	17.471	17.673
Acetonitrile	15.614	15.830	16.069	16.248	16.431	16.679	16.908	17.124
Toluene	18.525	18.681	18.851	18.987	19.131	19.298	19.458	19.613
Benzene	18.001	18.167	18.350	18.494	18.645	18.826	18.999	19.165
Methanol	14.897	15.127	15.383	15.573	15.765	16.034	16.280	16.511
Ethanol	15.613	15.829	16.068	16.247	16.430	16.678	16.908	17.123
Cyclohexane	18.484	18.640	18.811	18.948	19.092	19.260	19.421	19.578
Trichloroethylene	17.914	18.083	18.267	18.412	18.564	18.748	18.923	19.091
Tetrachloroethylene	17.914	18.083	18.267	18.412	18.564	18.748	18.923	19.091
Cellulose acrylate								
Solvents	303.15	308.15	313.15	318.15	323.15	328.15	333.15	338.15
n-Pentane	12.774	12.951	13.178	13.222	13.495	13.680	13.841	14.005
n-Hexane	16.096	16.109	16.140	16.071	16.229	16.135	16.181	16.187
n-Heptane	19.545	19.356	19.270	18.893	18.644	18.729	18.416	18.218
n-Octane	22.810	22.433	22.174	21.569	21.160	21.059	20.545	20.167
n-Nonane	26.187	25.672	25.194	24.592	24.112	23.638	23.096	22.582
CCl4	15.658	15.687	15.766	15.652	15.748	15.818	15.813	15.826
Nitromethane	8.276	8.694	9.147	9.440	9.993	10.353	10.782	11.180
CH2Cl2	8.119	8.546	9.007	9.308	9.871	10.237	10.676	11.082
Chloroform	11.520	11.766	12.056	12.169	12.522	12.754	12.993	13.222
Diethyl ether	10.960	11.237	11.554	11.699	12.086	12.340	12.612	12.870
THF	8.536	8.940	9.380	9.658	10.196	10.545	10.959	11.344
Ethyl acetate	10.882	11.163	11.484	11.632	12.025	12.282	12.558	12.820
Acetone	7.375	7.947	8.546	8.999	9.732	10.205	10.806	11.355
Acetonitrile	7.852	8.557	9.285	9.876	10.766	11.338	12.087	12.767

Toluene	14.344	14.442	14.588	14.546	14.723	14.845	14.917	14.999
Benzene	12.277	12.484	12.735	12.806	13.112	13.315	13.509	13.698
Methanol	7.996	8.852	9.723	10.472	11.539	12.223	13.141	13.970
Ethanol	8.835	9.541	10.269	10.861	11.752	12.325	13.075	13.757
Cyclohexane	14.201	14.306	14.460	14.425	14.612	14.739	14.820	14.909
Trichloroethylene	11.938	12.163	12.431	12.521	12.848	13.064	13.278	13.485
Tetrachloroethylene	15.803	15.824	15.896	15.773	15.860	15.925	15.911	15.917

Table S2. Variations of polar free energy $\Delta G_a^p(T)$ (in kJ/mol) of PLA and cellulose acrylate as a function of temperature.

PLA								
Solvents	303.15	308.15	313.15	318.15	323.15	328.15	333.15	338.15
CCl4	1.925	1.828	1.731	1.634	1.537	1.440	1.343	1.246
Nitromethane	13.400	12.725	12.050	11.376	10.701	10.026	9.351	8.677
CH2Cl2	11.002	10.331	9.661	8.990	8.320	7.649	6.979	6.308
Chloroform	15.651	14.863	14.074	13.286	12.497	11.709	10.920	10.132
Diethyl ether	11.305	10.738	10.170	9.603	9.035	8.468	7.900	7.333
THF	9.732	9.266	8.801	8.335	7.870	7.404	6.939	6.473
Ethyl acetate	4.397	3.860	3.323	2.786	2.249	1.712	1.175	0.638
Acetone	5.637	5.371	5.105	4.839	4.573	4.307	4.041	3.775
Acetonitrile	18.933	17.980	17.028	16.076	15.124	14.171	13.219	12.267
Toluene	10.359	10.018	9.677	9.336	8.995	8.654	8.313	7.972
Benzene	0.540	0.513	0.485	0.458	0.431	0.404	0.377	0.349
Methanol	40.830	39.913	38.996	38.078	37.161	36.244	35.327	34.409
Ethanol	29.396	28.629	27.862	27.095	26.328	25.561	24.794	24.027
Cyclohexane	2.967	2.818	2.668	2.519	2.369	2.220	2.070	1.921
Trichloroethylene	2.376	2.256	2.136	2.017	1.897	1.778	1.658	1.538
Tetrachloroethylene	3.072	2.917	2.763	2.608	2.454	2.299	2.144	1.990
Cellulose acrylate								
Solvents	303.15	308.15	313.15	318.15	323.15	328.15	333.15	338.15

CCl4	6.894	6.823	6.752	6.681	6.610	6.539	6.468	6.398
Nitromethane	7.961	6.840	5.719	4.598	3.477	2.356	1.235	0.114
CH2Cl2	36.353	35.841	35.329	34.816	34.304	33.791	33.279	32.766
Chloroform	9.266	9.003	8.740	8.477	8.214	7.951	7.688	7.425
Diethyl ether	11.996	11.424	10.852	10.280	9.708	9.136	8.564	7.992
THF	15.084	14.710	14.335	13.961	13.586	13.212	12.837	12.463
Ethyl acetate	18.478	17.949	17.420	16.890	16.361	15.832	15.303	14.774
Acetone	39.244	38.650	38.056	37.462	36.868	36.274	35.680	35.086
Acetonitrile	47.955	47.282	46.609	45.937	45.264	44.591	43.919	43.246
Toluene	15.987	15.686	15.384	15.083	14.781	14.480	14.178	13.877
Benzene	1.829	1.809	1.789	1.768	1.748	1.727	1.707	1.687
Methanol	72.172	71.461	70.750	70.039	69.328	68.617	67.905	67.194
Ethanol	54.951	54.331	53.712	53.093	52.474	51.855	51.235	50.616
Cyclohexane	10.421	10.309	10.197	10.085	9.973	9.861	9.749	9.637
Trichloroethylene	7.697	7.605	7.514	7.422	7.330	7.238	7.147	7.055
Tetrachloroethylene	10.235	10.124	10.014	9.903	9.793	9.683	9.572	9.462

Table S3. Variations of the separation distance r(T) between solvents and polymer surfaces as a function of temperature.

PLA								
Temperature (K)	303.15	308.15	313.15	318.15	323.15	328.15	333.15	338.15
n-Pentane	5.737	5.727	5.717	5.709	5.702	5.691	5.680	5.671
n-Hexane	5.661	5.655	5.650	5.644	5.638	5.633	5.629	5.624
n-Heptane	5.587	5.583	5.579	5.576	5.572	5.569	5.566	5.562
n-Octane	5.580	5.577	5.574	5.571	5.568	5.565	5.562	5.559
n-Nonane	5.541	5.538	5.536	5.533	5.531	5.528	5.525	5.523
CCl4	5.825	5.817	5.809	5.802	5.795	5.787	5.780	5.773
Nitromethane	5.540	5.530	5.519	5.510	5.502	5.491	5.481	5.472
CH2Cl2	5.532	5.522	5.511	5.502	5.494	5.483	5.473	5.463

Chloroform	5.681	5.672	5.662	5.655	5.647	5.637	5.628	5.620
Diethyl ether	5.660	5.651	5.641	5.633	5.625	5.616	5.606	5.598
THF	5.554	5.544	5.533	5.524	5.516	5.505	5.495	5.486
Ethyl acetate	5.657	5.647	5.637	5.630	5.622	5.612	5.603	5.594
Acetone	5.382	5.371	5.359	5.350	5.341	5.329	5.318	5.308
Acetonitrile	5.205	5.193	5.180	5.171	5.161	5.148	5.137	5.126
Toluene	5.784	5.776	5.768	5.761	5.753	5.745	5.737	5.730
Benzene	5.711	5.703	5.693	5.686	5.678	5.669	5.660	5.652
Methanol	4.938	4.926	4.912	4.902	4.892	4.878	4.866	4.855
Ethanol	5.205	5.193	5.180	5.171	5.161	5.148	5.136	5.126
Cyclohexane	5.779	5.771	5.762	5.755	5.748	5.739	5.731	5.724
Trichloroethylene	5.699	5.690	5.680	5.673	5.665	5.656	5.647	5.638
Tetrachloroethylene	5.882	5.873	5.863	5.855	5.847	5.838	5.829	5.820
Cellulose acrylate								
Solvents	303.15	308.15	313.15	318.15	323.15	328.15	333.15	338.15
n-Pentane	6.607	6.589	6.566	6.562	6.536	6.518	6.504	6.489
n-Hexane	6.495	6.494	6.492	6.497	6.485	6.492	6.489	6.488
n-Heptane	6.393	6.404	6.409	6.433	6.449	6.444	6.464	6.477
n-Octane	6.369	6.388	6.402	6.434	6.457	6.463	6.492	6.515
n-Nonane	6.297	6.320	6.341	6.369	6.392	6.415	6.442	6.469
CCl4	6.502	6.500	6.493	6.502	6.495	6.489	6.490	6.489
Nitromethane	6.918	6.844	6.770	6.725	6.645	6.597	6.542	6.493
CH2Cl2	6.935	6.858	6.781	6.733	6.650	6.600	6.543	6.494
Chloroform	6.671	6.643	6.611	6.598	6.561	6.537	6.513	6.491
Diethyl ether	6.704	6.670	6.632	6.616	6.573	6.545	6.517	6.491
THF	6.892	6.823	6.754	6.712	6.637	6.591	6.539	6.493
Ethyl acetate	6.708	6.674	6.635	6.618	6.574	6.547	6.518	6.491
Acetone	6.846	6.731	6.624	6.551	6.443	6.380	6.305	6.242
Acetonitrile	6.486	6.365	6.254	6.173	6.064	6.000	5.924	5.860
Toluene	6.545	6.537	6.524	6.528	6.512	6.502	6.496	6.489

Benzene	6.632	6.610	6.584	6.577	6.546	6.526	6.508	6.490
Methanol	6.080	5.946	5.829	5.740	5.627	5.563	5.484	5.418
Ethanol	6.319	6.216	6.121	6.051	5.955	5.899	5.830	5.773
Cyclohexane	6.551	6.541	6.528	6.531	6.514	6.504	6.497	6.489
Trichloroethylene	6.649	6.624	6.596	6.586	6.553	6.531	6.510	6.491
Tetrachloroethylene	6.497	6.496	6.490	6.500	6.493	6.488	6.489	6.488

Table S4. Variations of the surface area ($Å^2$) of adsorbed solvents on zeolite surfaces as a function temperature for PLA and CA.

PLA								
Solvents	303.15	308.15	313.15	318.15	323.15	328.15	333.15	338.15
n-Pentane	41.0	42.5	44.1	45.6	47.2	49.2	51.2	53.3
n-Hexane	48.8	50.1	51.4	52.9	54.5	56.0	57.7	59.4
n-Heptane	56.8	58.1	59.5	60.9	62.3	63.9	65.5	67.2
n-Octane	63.9	65.2	66.6	68.1	69.6	71.1	72.8	74.5
n-Nonane	70.2	71.6	73.0	74.4	76.0	77.6	79.2	81.0
CCl4	33.0	33.9	34.8	35.6	36.5	37.5	38.5	39.6
Nitromethane	30.0	31.0	32.1	33.2	34.3	35.6	37.0	38.4
CH2 Cl2	28.9	29.8	30.7	31.7	32.6	33.8	34.9	36.1
Chloroform	30.7	31.6	32.5	33.4	34.4	35.4	36.5	37.6
Diethyl ether	41.9	43.4	45.1	46.8	48.6	50.7	52.8	55.2
THF	29.6	30.5	31.4	32.3	33.2	34.3	35.4	36.5
Ethyl acetate	34.6	35.4	36.4	37.3	38.2	39.3	40.3	41.4
Acetone	32.8	33.8	34.8	35.8	36.9	38.1	39.3	40.5
Acetonitrile	30.2	31.3	32.5	33.7	34.9	36.3	37.8	39.3
Toluene	31.8	32.5	33.2	33.8	34.5	35.3	36.1	36.8
Benzene	30.4	31.2	32.0	32.9	33.7	34.7	35.7	36.7
Methanol	28.1	29.0	29.9	30.7	31.6	32.7	33.7	34.7
Ethanol	30.5	31.4	32.4	33.3	34.3	35.4	36.5	37.6

Cyclohexane	33.4	34.3	35.2	36.1	37.1	38.1	39.2	40.3
Trichloroethylene	37.5	38.3	39.2	40.1	40.9	41.9	42.9	43.9
Tetrachloroethylene	32.4	33.0	33.7	34.3	35.0	35.7	36.4	37.2
Cellulose acrylate								
Solvents	303.15	308.15	313.15	318.15	323.15	328.15	333.15	338.15
n-Pentane	32.2	33.5	35.1	36.2	38.0	39.7	41.5	43.4
n-Hexane	37.7	38.6	39.5	40.3	41.7	42.5	43.8	45.0
n-Heptane	43.5	44.0	44.7	44.8	45.2	46.4	46.8	47.4
n-Octane	48.9	49.0	49.4	49.1	49.1	49.9	49.8	49.9
n-Nonane	54.4	54.3	54.3	54.1	54.1	54.0	53.9	53.8
CCl4	30.3	30.9	31.6	32.0	32.9	33.7	34.4	35.2
Nitromethane	16.1	17.4	18.7	19.8	21.5	22.9	24.5	26.2
CH2 Cl2	15.3	16.4	17.7	18.7	20.3	21.5	23.0	24.5
Chloroform	21.9	22.9	23.9	24.6	25.9	27.0	28.1	29.3
Diethyl ether	28.7	30.2	32.0	33.4	35.6	37.5	39.7	42.0
THF	16.3	17.5	18.7	19.7	21.2	22.4	23.8	25.2
Ethyl acetate	23.5	24.5	25.7	26.5	27.9	29.0	30.2	31.5
Acetone	16.4	18.0	19.7	21.2	23.4	25.0	27.1	29.1
Acetonitrile	16.7	18.7	20.8	22.7	25.4	27.5	30.1	32.8
Toluene	27.1	27.7	28.4	28.7	29.5	30.2	30.8	31.5
Benzene	22.8	23.7	24.6	25.2	26.4	27.3	28.3	29.3
Methanol	16.6	18.7	20.9	22.9	25.7	27.7	30.3	32.8
Ethanol	19.0	20.9	22.9	24.7	27.2	29.1	31.5	33.8
Cyclohexane	28.3	29.0	29.9	30.5	31.5	32.5	33.4	34.3
Trichloroethylene	27.5	28.5	29.5	30.2	31.5	32.5	33.6	34.7
Tetrachloroethylene	31.5	31.9	32.4	32.6	33.2	33.7	34.1	34.6

Table S5. Values of London dispersive surface energy of polymer surfaces as a function of temperature

T(K)	PLA	Cellulose acrylate

303.15	88.19	72.60
308.15	87.196	71.519
313.15	86.196	70.477
318.15	85.184	69.285
323.15	84.161	68.208
328.15	83.131	67.162
333.15	82.086	66.004
338.15	81.032	64.870