

Shared Depletion and Re-stabilization Colloidal Interactions in Phase Diagrams for Silica Nanoparticle and Asphaltene + Polystyrene + Solvent Mixtures

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Supporting Information

Experimental data sets for relative phase volumes, phase boundary enclosing gas (G) and liquid (L) phases at equilibrium and critical points for nano-silica + polystyrene (237 kg/mol) + cyclohexane are reported at 296 K, 303 K, and 313 K as Tables S1a-c, Table S2a-c and Table S3a-c respectively.

Cloud points data for polystyrene + cyclohexane, polystyrene + cyclohexane + toluene, polystyrene + cyclohexane + heptane, and polystyrene + cyclohexane + water are reported in Tables S4, S5, S6, and S7 respectively.

Compositions and associated polymer-rich phase volume data for Athabasca retentate + polystyrene (400 kg/mol) + toluene (based on X-ray measurements) for trajectories p, q, and r are reported in Table S8. Computed binodal points for this ternary, based on X-ray measurements, are reported in Table S9.

Table S.10: Compositions and associated polymer-rich phase volume data for pentane asphaltene + polystyrene + toluene (based on X-ray measurements) for trajectories 1, 2, 3, 4, 5, 6, 7

Compositions and associated polymer-rich phase volume data for pentane asphaltene + polystyrene + toluene for trajectories p, q, and r (based on X-ray measurements) and computed binodal points, using the method of Bondar et al.⁴⁰ are listed in Table S 11 and S 13 respectively.

Table S 12: Compositions and associated polymer-rich phase volume data for retentate + polystyrene + toluene (based on X-Ray measurements) for seven composition trajectories.

Table S1a Polymer-Rich Phase Volume Fraction Data at 296 K

Polystyrene mass fraction ± 0.0005	Nano silica mass fraction ± 0.0005	Cyclohexane mass fraction ± 0.0005	volume fraction of polymer rich phase (R_1) ± 0.03
0.0002	0.0000	0.9998	1.0000
0.0002	0.0013	0.9986	0.8500
0.0002	0.0028	0.9970	0.5500
0.0002	0.0044	0.9954	0.0000
0.0039	0.0000	0.9961	1.0000
0.0039	0.0033	0.9927	0.6800
0.0039	0.0061	0.9900	0.1100
0.0039	0.0066	0.9895	0.0000
0.0105	0.0000	0.9895	1.0000
0.0104	0.0011	0.9885	0.8900
0.0101	0.0031	0.9868	0.7300
0.0101	0.0056	0.9843	0.5700
0.0101	0.0095	0.9805	0.2100
0.0100	0.0110	0.9790	0.0400
0.0095	0.0000	0.9905	1.0000
0.0095	0.0008	0.9897	0.8200
0.0095	0.0033	0.9872	0.5700
0.0094	0.0081	0.9825	0.0000
0.0500	0.0000	0.9500	0.8800
0.0515	0.0003	0.9483	0.8700
0.0512	0.0051	0.9437	0.7800
0.0507	0.0131	0.9362	0.5100
0.0506	0.0168	0.9326	0.3500
0.0504	0.0215	0.9281	0.2600

0.0502	0.0249	0.9249	0.1400
0.0500	0.0278	0.9222	0.0750
0.0500	0.0300	0.9200	0.0000
0.1000	0.0000	0.9000	0.6700
0.1000	0.0100	0.8900	0.6710
0.0980	0.0145	0.8875	0.6200
0.0960	0.0250	0.8790	0.5300
0.0970	0.0290	0.8740	0.3600
0.0960	0.0360	0.8680	0.1200
0.0970	0.0430	0.8600	0.0760
0.0950	0.0530	0.8520	0.0310
0.1500	0.0000	0.8500	0.3500
0.1463	0.0013	0.8524	0.3400
0.1461	0.0029	0.8510	0.3200
0.1452	0.0069	0.8479	0.3300
0.1440	0.0176	0.8384	0.2660
0.1677	0.0220	0.8103	0.2400
0.1427	0.0263	0.8310	0.1300
0.1410	0.0377	0.8213	0.0000
0.2121	0.0000	0.7879	0.0730
0.2100	0.0006	0.7894	0.0700
0.2116	0.0024	0.7860	0.0580
0.2107	0.0068	0.7825	0.0800
0.2099	0.0109	0.7792	0.0820
0.2088	0.0161	0.7752	0.0400
0.2079	0.0201	0.7720	0.0380
0.2066	0.0260	0.7674	0.0220

Table S1b LG/G and LG/L Phase Boundary Data at 296 K

Nano silica mass fraction ± 0.0005	Polystyrene mass fraction ± 0.0005	Cyclohexane mass fraction ± 0.0005
0.0044	0.0016	0.9940
0.0066	0.0039	0.9895
0.0110	0.0100	0.9790
0.0300	0.0500	0.9200
0.0530	0.0950	0.8520
0.0377	0.1410	0.8213
0.0260	0.2066	0.7674
0.0000	0.2300	0.7700
0.0000	0.0200	0.9800
0.0002	0.0001	0.9997
0.0002	0.0000	0.9998
0.0043	0.0001	0.9956

Table S1c L=G Critical Point at 296 K

Nano silica mass fraction	Polystyrene mass fraction	Cyclohexane mass fraction
0.0030 ± 0.00005	0.0002 ± 0.00005	0.9968 ± 0.00005

Table S2a Polymer-Rich Phase Volume Fraction Data at 303 K

Nano silica mass fraction ± 0.0005	Polystyrene mass fraction ± 0.0005	Cyclohexane mass fraction ± 0.0005	volume fraction of polymer rich phase (R_1) ± 0.03
0.0000	0.0002	0.9998	1.0000
0.0013	0.0002	0.9986	0.8400
0.0028	0.0002	0.9970	0.5800
0.0044	0.0016	0.9940	0.0000

0.0000	0.0039	0.9961	1.0000
0.0033	0.0039	0.9927	0.7000
0.0061	0.0039	0.9900	0.1200
0.0066	0.0039	0.9895	0.0000
0.0000	0.0105	0.9895	1.0000
0.0011	0.0104	0.9885	0.9200
0.0031	0.0101	0.9868	0.7800
0.0056	0.0101	0.9843	0.4980
0.0095	0.0101	0.9805	0.2500
0.0110	0.0100	0.9790	0.0300
0.0000	0.0095	0.9905	1.0000
0.0008	0.0095	0.9897	0.8500
0.0033	0.0095	0.9872	0.6300
0.0081	0.0094	0.9825	0.0000
0.0000	0.0200	0.9800	1.0000
0.0010	0.0200	0.9790	0.9900
0.0034	0.0200	0.9767	0.7300
0.0128	0.0198	0.9674	0.1500
0.0143	0.0197	0.9660	0.1000
0.0172	0.0197	0.9631	0.0000
0.0000	0.0500	0.9500	1.0000
0.0003	0.0515	0.9483	1.0000
0.0051	0.0512	0.9437	0.7700
0.0131	0.0507	0.9362	0.3600
0.0168	0.0506	0.9326	0.2700
0.0215	0.0504	0.9281	0.2300
0.0249	0.0502	0.9249	0.1300
0.0278	0.0500	0.9222	0.0780

0.0300	0.0500	0.9200	0.0000
0.0000	0.1000	0.9000	1.0000
0.0100	0.1000	0.8900	0.6800
0.0145	0.0980	0.8875	0.5500
0.0250	0.0960	0.8790	0.2400
0.0290	0.0970	0.8740	0.0400
0.0360	0.0960	0.8680	0.0000
0.0000	0.1500	0.8500	1.0000
0.0013	0.1463	0.8524	0.9730
0.0029	0.1461	0.8510	0.7430
0.0069	0.1452	0.8479	0.6870
0.0176	0.1440	0.8384	0.5230
0.0220	0.1677	0.8103	0.3170
0.0263	0.1427	0.8310	0.0000
0.0000	0.2121	0.7879	1.0000
0.0006	0.2100	0.7894	0.9250
0.0024	0.2116	0.7860	0.7620
0.0068	0.2107	0.7825	0.4600
0.0109	0.2099	0.7792	0.2600
0.0161	0.2088	0.7752	0.0100
0.0012	0.2621	0.7367	1.0000
0.0097	0.2598	0.7305	0.2300
0.0123	0.2592	0.7285	0.0000

Table S2b LG/G and LG/L Phase Boundary Data at 303 K

Nano silica mass fraction ± 0.0005	Polystyrene mass fraction ± 0.0005	Cyclohexane mass fraction ± 0.0005
0.0044	0.0016	0.9940
0.0066	0.0039	0.9895

0.0110	0.0100	0.9790
0.0172	0.0197	0.9631
0.0300	0.0500	0.9200
0.0360	0.0960	0.8680
0.0263	0.1430	0.8307
0.0161	0.2080	0.7759
0.0123	0.2590	0.7287
0.0012	0.2621	0.7367
0.0003	0.0515	0.9483
0.0002	0.0001	0.9997
0.0002	0.0000	0.9998
0.0043	0.0001	0.9956
0.0045	0.0007	0.9947
0.0066	0.0039	0.9895

Table S2c L=G Critical Points at 303 K

Nano silica mass fraction	Polystyrene mass fraction	Cyclohexane mass fraction
0.0030 \pm 0.00005	0.0002 \pm 0.00005	0.9968 \pm 0.00005
0.0040 \pm 0.0005	0.2750 \pm 0.0005	0.7210 \pm 0.0005

Table S3a Polymer-Rich Phase Volume Fraction Data at 313 K			
Nano silica mass fraction \pm 0.0005	Polystyrene mass fraction \pm 0.0005	Cyclohexane mass fraction \pm 0.0005	volume fraction of polymer rich phase (R_1) \pm 0.03
0.0021	0.0022	0.9957	0.8740
0.0046	0.0022	0.9932	0.0000
0.9860	0.0097	0.0043	0.6811
0.9813	0.0097	0.0090	0.5011

0.9768	0.0096	0.0135	0.2200
0.8866	0.1069	0.0065	0.8095
0.8803	0.1061	0.0136	0.5646
0.8752	0.1055	0.0193	0.3110
0.8716	0.1051	0.0233	0.1752
0.8025	0.1899	0.0076	0.5842
0.7999	0.1893	0.0108	0.3794
0.7981	0.1889	0.0130	0.2378
0.7993	0.1939	0.0068	0.7136
0.7939	0.1926	0.0136	0.3456
0.7557	0.0042	0.2401	1.0000

Table S3b LG/G and LG/L Phase Boundary Data at 313 K

Nano silica mass fraction ± 0.0005	Polystyrene mass fraction ± 0.0005	Cyclohexane mass fraction ± 0.0005
0.0017	0.0022	0.9961
0.0046	0.0022	0.9932
0.0182	0.0096	0.9722
0.0277	0.1046	0.8677
0.0167	0.1882	0.7951
0.0049	0.2802	0.7149
0.0010	0.1912	0.8078
0.0014	0.1074	0.8912
0.0010	0.0098	0.9892

Table S3c L=G Critical Points at 313 K

Nano silica mass fraction	Polystyrene mass fraction	Cyclohexane mass fraction
0.0042 ± 0.0005	0.2601 ± 0.0005	0.7357 ± 0.0005
0.0030 ± 0.00005	0.0002 ± 0.00005	0.9968 ± 0.00005

Table S4 Cloud Point Data for Cyclohexane + Polystyrene (237 kg/mol) Binary

Polystyrene mass fraction ± 0.005	Temperature (K) ± 0.20
0.01	296.56
0.0267	298.46
0.05	298.56
0.087	298.66
0.1	298.56
0.138	298.26
0.198	297.86

Table S5a Cloud Point Data for Cyclohexane + Polystyrene (237 kg/mol) + Toluene (1 mass %)

Polystyrene mass fraction ± 0.005	Temperature (K) ± 0.20
0.01	294.26
0.0267	296.36
0.05	296.46
0.1	296.66
0.15	296.16

Table S5b Cloud Point Data for Cyclohexane + Polystyrene (237 kg/mol) + Toluene (5 mass %)

Polystyrene mass fraction ± 0.005	Temperature (K) ± 0.20
0.01	287.06
0.0267	289.06
0.05	289.06
0.1	289.26
0.15	288.06

Table S6a Cloud Point Data for Cyclohexane + Polystyrene (237 kg/mol) + Heptane (4.5 mass %)

Polystyrene mass fraction \pm 0.005	Temperature (K) \pm 0.20
0.01	302.16
0.05	302.7
0.0874	303.96
0.1987	303.26

Table S6b Cloud Point Data for Cyclohexane + Polystyrene (237 kg/mol) + Heptane (8.3 mass %)

Polystyrene mass fraction \pm 0.005	Temperature (K) \pm 0.20
0.01	302.16
0.05	302.7
0.0874	303.96
0.1987	303.26

Table S7 Cloud Point Data for Cyclohexane + Polystyrene (237 kg/mol) + Water (saturated)

Polystyrene mass fraction \pm 0.005	Temperature (K) \pm 0.20
0.01	297.76
0.0267	299.66
0.05	299.76
0.0874	299.86
0.1	299.76
0.1384	299.46

Table S.8: Compositions and associated polymer-rich phase volume data for Athabasca retentate + polystyrene + toluene (based on X-ray measurements) for trajectories p, q, and r

	Asphaltene volume fraction	Asphaltene mass fraction	Polystyrene volume fraction	Polystyrene mass fraction	Volume fraction of the upper phase (R ₁)
p	0.053	0.069	0.071	0.083	0.760
	0.048	0.063	0.064	0.076	0.775
	0.044	0.058	0.059	0.070	0.798
	0.039	0.052	0.052	0.062	0.829
	0.034	0.045	0.045	0.054	0.880
	0.030	0.040	0.040	0.048	0.911
q	0.100	0.128	0.043	0.050	0.371
	0.093	0.120	0.040	0.046	0.393
	0.085	0.110	0.036	0.042	0.427
	0.075	0.098	0.032	0.037	0.484
	0.070	0.092	0.030	0.035	0.517
	0.063	0.083	0.027	0.032	0.576
r	0.13	0.164	0.03	0.034	0.13
	0.12	0.153	0.02	0.023	0.16
	0.10	0.129	0.02	0.023	0.19
	0.09	0.117	0.02	0.023	0.24
	0.08	0.104	0.02	0.023	0.29

Table S.9: Computed binodal points for Athabasca retentate + polystyrene + toluene based on X-ray measurements for composition trajectories p, q, r in Table S.8 and the method of Bondar et al.⁴⁰

Asphaltene volume fraction	Polystyrene volume fraction
0.020	0.066
0.021	0.050
0.021	0.058
0.021	0.074
0.022	0.082
0.023	0.042
0.118	0.011
0.125	0.013
0.129	0.012
0.135	0.013
0.139	0.013
0.142	0.013

Table S.10: Compositions and associated polymer-rich phase volume data for pentane asphaltene + polystyrene + toluene (based on X-ray measurements) for trajectories 1, 2, 3, 4, 5, 6, 7

1				
Asphaltene volume fraction	Asphaltene mass fraction	Polymer volume fraction	Polymer mass fraction	R ₁ (upper phase volume fraction)
0.040	0.054	0.034	0.041	0.900
0.049	0.066	0.033	0.039	0.820
0.076	0.101	0.032	0.038	0.650
0.100	0.131	0.032	0.037	0.500
0.112	0.147	0.031	0.036	0.440
0.148	0.191	0.030	0.034	0.310
0.170	0.218	0.029	0.033	0.170
0.185	0.236	0.029	0.033	0.100
2				
Asphaltene volume fraction	Asphaltene mass fraction	Polymer volume fraction	Polymer mass fraction	R ₁ (upper phase volume fraction)
0.048	0.064	0.067	0.079	0.860
0.066	0.087	0.065	0.076	0.700
0.091	0.119	0.064	0.075	0.590
0.130	0.168	0.061	0.070	0.490
0.190	0.241	0.057	0.064	0.320
0.243	0.303	0.053	0.059	0.200
0.299	0.366	0.049	0.053	0.150
3				
Asphaltene volume fraction		Polymer volume fraction		R ₁ (upper phase volume fraction)

0.053	0.070	0.114	0.133	0.870
0.156	0.198	0.105	0.119	0.590
0.167	0.211	0.104	0.117	0.557
0.179	0.226	0.102	0.114	0.520
0.218	0.271	0.098	0.109	0.440
0.280	0.342	0.090	0.098	0.280
0.300	0.364	0.088	0.095	0.180
0.190	0.239	0.101	0.113	0.500
0.317	0.383	0.085	0.091	0.130

4

Asphaltene volume fraction	Asphaltene mass fraction	Polymer volume fraction	Polymer mass fraction	R ₁ (upper phase volume fraction)
0.125	0.158	0.175	0.197	0.840
0.158	0.198	0.168	0.187	0.690
0.196	0.243	0.161	0.177	0.580
0.270	0.327	0.146	0.157	0.380
0.230	0.282	0.154	0.168	0.500
0.280	0.338	0.144	0.155	0.350
0.290	0.349	0.142	0.152	0.310
0.310	0.371	0.138	0.147	0.240
0.330	0.393	0.134	0.142	0.180

5

Asphaltene volume fraction	Asphaltene mass fraction	Polymer volume fraction	Polymer mass fraction	R ₁ (upper phase volume fraction)
0.160	0.197	0.240	0.263	0.850
0.200	0.244	0.231	0.251	0.700
0.244	0.294	0.220	0.236	0.546
0.260	0.312	0.215	0.229	0.510
0.330	0.388	0.200	0.209	0.320

0.352	0.412	0.190	0.198	0.230
0.370	0.431	0.185	0.192	0.160

6				
Asphaltene volume fraction	Asphaltene mass fraction	Polymer volume fraction	Polymer mass fraction	R ₁ (upper phase volume fraction)
0.300	0.350	0.291	0.302	0.460
0.280	0.330	0.272	0.285	0.480
0.250	0.299	0.243	0.259	0.540
0.240	0.289	0.233	0.249	0.570
0.230	0.278	0.223	0.240	0.590

7				
Asphaltene volume fraction	Asphaltene mass fraction	Polymer volume fraction	Polymer mass fraction	R ₁ (upper phase volume fraction)
0.41	0.422	0.296	0.300	0.310
0.39	0.403	0.280	0.287	0.350

Table S.11: Compositions and associated polymer-rich phase volume data for pentane asphaltene + polystyrene + toluene (based on X-ray measurements) for trajectories p, q, and r.

	Asphaltene volume fraction	Asphaltene mass fraction	Polystyrene volume fraction	Polystyrene mass fraction	Volume fraction of the upper phase (R)
p	0.065	0.086	0.042	0.050	0.754
	0.059	0.079	0.039	0.046	0.797
	0.055	0.073	0.035	0.042	0.850
	0.050	0.067	0.033	0.039	0.896
	0.047	0.063	0.030	0.036	0.930
	0.044	0.059	0.028	0.033	0.956
q	0.103	0.135	0.030	0.035	0.464
	0.094	0.124	0.028	0.033	0.505
	0.086	0.114	0.025	0.029	0.553
	0.079	0.105	0.023	0.027	0.615
	0.074	0.098	0.022	0.026	0.650
	0.069	0.092	0.020	0.024	0.689
r	0.130	0.169	0.024	0.028	0.282
	0.119	0.156	0.022	0.026	0.313
	0.110	0.144	0.020	0.024	0.346
	0.100	0.132	0.018	0.022	0.370
	0.094	0.124	0.017	0.020	0.393
	0.088	0.117	0.016	0.019	0.422

Table S 12: Compositions and associated polymer-rich phase volume data for retentate + polystyrene + toluene (based on X-Ray measurements) for trajectories 1, 2, 3, 4, 5, 6, 7

1				
Asphaltene volume fraction	Asphaltene mass fraction	Polymer volume fraction	Polymer mass fraction	R ₁ (upper phase volume fraction)
0.030	0.040	0.044	0.044	0.850
0.048	0.063	0.043	0.043	0.670
0.070	0.091	0.042	0.042	0.530
0.080	0.104	0.041	0.041	0.470
0.112	0.143	0.040	0.04	0.390
0.140	0.176	0.039	0.039	0.330
0.172	0.212	0.037	0.037	0.290
0.211	0.255	0.036	0.036	0.160

2				
Asphaltene volume fraction	Asphaltene mass fraction	Polymer volume fraction	Polymer mass fraction	R ₁ (upper phase volume fraction)
0.037	0.049	0.091	0.091	0.850
0.070	0.090	0.088	0.088	0.680
0.100	0.127	0.085	0.085	0.570
0.120	0.151	0.083	0.083	0.500
0.190	0.230	0.076	0.076	0.280
0.211	0.253	0.075	0.075	0.200
0.240	0.284	0.071	0.071	0.130

3

Asphaltene volume fraction	Asphaltene mass fraction	Polymer volume fraction	Polymer mass fraction	R_1 (upper phase volume fraction)
0.050	0.065	0.138	0.138	0.880
0.080	0.102	0.133	0.133	0.730
0.120	0.150	0.127	0.127	0.580
0.160	0.195	0.121	0.121	0.460
0.200	0.239	0.115	0.115	0.320
0.240	0.282	0.109	0.109	0.200
0.260	0.302	0.106	0.106	0.140

4

Asphaltene volume fraction	Asphaltene mass fraction	Polymer volume fraction	Polymer mass fraction	R_1 (upper phase volume fraction)
0.100	0.124	0.188	0.188	0.920
0.120	0.148	0.184	0.184	0.810
0.150	0.182	0.178	0.178	0.670
0.190	0.226	0.169	0.169	0.460
0.220	0.258	0.163	0.163	0.320
0.250	0.289	0.158	0.158	0.160
0.265	0.304	0.153	0.153	0.100

5

Asphaltene volume fraction	Asphaltene mass fraction	Polymer volume fraction	Polymer mass fraction	R_1 (upper phase volume fraction)
0.230	0.267	0.182	0.182	0.310
0.220	0.258	0.174	0.174	0.290

6

Asphaltene volume fraction	Asphaltene mass fraction	Polymer volume fraction	Polymer mass fraction	R_1 (upper phase volume fraction)
0.210	0.245	0.215	0.215	0.470
0.195	0.230	0.199	0.199	0.440

7

Asphaltene volume fraction	Asphaltene mass fraction	Polymer volume fraction	Polymer mass fraction	R_1 (upper phase volume fraction)
0.115	0.142	0.198	0.198	0.800
0.105	0.130	0.181	0.181	0.840

Table S.13: Computed binodal points for pentane asphaltene + polystyrene + toluene based on X-ray measurements for trajectories p, q, r in Table S.11 and the method of Bondar et al.⁴⁰

Asphaltene volume fraction	Polystyrene volume fraction
0.034	0.058
0.035	0.066
0.036	0.050
0.036	0.042
0.038	0.035
0.039	0.028
0.138	0.013
0.144	0.012
0.153	0.011
0.158	0.010
0.168	0.010
0.176	0.010