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Gel Lattice Alters the Phase State of the Solvent

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Some low-molecular-weight substances are able to self-assemble into the fiber-like structures (strings) to form gels. One of the examples of such substances is trifluoroacetylated *alpha*-aminoalcohols (TFAAAs) able of gelation of many organic solvents. Here we report formation and describe the properties of a layer of an altered solvent covering the strings' surface. The altered solvent layer has a different refractive index and melts at a temperature about several degrees lower than the bulk solvent. Moreover, the bulk solvent's melting temperature was also depressed by values far beyond the one expected according to Raoult's law. Based on the Gibbs–Thomson equation it is possible to derive the thickness of the special layer as well as the average gel lattice parameters, which were very stable across the variety of the systems investigated.

Supplementary materials

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Table S1 The experimental data on the phase transition temperatures (K) / enthalpies (J/g) for TFAAA solutions in heptane. T_{fH} – fusion temperature, T_{cH} – crystallization temperature. T'_{fH} and T'_{cH} — denote the position of the satellite peaks below T_f and T_c.

	C, mg/ml	T_{cH}	T'_{cH}	T_{fH}	T'_{fH}
Pure Heptane		175.0 ± 0.3 117.8 ± 0.5	–	185.1 ± 0.4 -129.5 ± 1.6	–
TFAAA-4	0.10	175.1 / 104.9	166.4 / 2.2	184.4 / −111.6	174.4 / −6.0
	0.10	175.7 / 106.2	166.4 / 2.4	184.3 / −110.7	175.0 / −8.1
	0.40	174.0 / 104.9	168.7 / 8.2	183.4 / −103.8	175.3 / −21.1
	0.40	174.4 / 106.5	168.7 / 7.9	183.4 / −99.0	175.4 / −21.0
	1.0	173.7 / 102.1	168.6 / 11.0	183.2 / −102.0	175.5 / −21.4
	1.0	173.5 / 100.0	168.3 / 10.8	183.2 / −99.4	175.5 / −21.9
	mean	174.3 ± 0.8 104.1 ± 2.3	167.8 ± 1.0 7.1 ± 3.6	183.6 ± 0.5 -104.4 ± 5.0	175.1 ± 0.4 -16.6 ± 6.8
TFAAA-5	0.05	174.1 / 120.3	167.7 / 5.4	183.6 / −124.3	174.8 / −13.6
	0.05	173.5 / 113.5	167.8 / 5.1	183.5 / −117.5	174.8 / −13.7
	0.20	175.1 / 113.3	165.7 / 1.8	184.6 / −120.1	175.0 / −5.9
	0.20	174.6 / 115.9	165.9 / 1.8	184.2 / −122.2	174.8 / −6.1
	1.0	175.7 / 103.7	167.4 / 4.0	183.8 / −108.1	174.8 / −10.2
	1.0	175.5 / 111.3	167.4 / 4.3	183.8 / −115.6	174.9 / −11.2
	mean	174.8 ± 0.7 113.2 ± 4.7	166.9 ± 0.8 3.5 ± 1.4	183.8 ± 0.4 -118.4 ± 5.0	174.7 ± 0.3 -9.7 ± 3.1
TFAAA-6	0.05	174.1 / 110.0	167.9 / 4.8	183.4 / −116.5	174.7 / −12.7
	0.05	173.8 / 107.1	167.9 / 5.2	183.5 / −111.8	174.8 / −13.0
	0.20	174.1 / 98.8	168.1 / 4.4	183.1 / −101.4	174.5 / −10.1
	0.20	173.9 / 108.0	168.0 / 5.3	183.3 / −111.4	174.7 / −13.12
	1.0	174.7 / 106.8	168.1 / 5.8	183.6 / −110.4	174.1 / −15.6
	1.0	174.8 / 125.0	168.2 / 6.8	183.5 / −129.4	174.9 / −16.7
	mean	174.2 ± 0.4 109.3 ± 7.9	168.0 ± 0.1 5.4 ± 0.8	183.3 ± 0.2 -113.5 ± 8.4	174.7 ± 0.2 -13.5 ± 2.1
TFAAA-7	0.005	171.9 / 85.9	169.0 / 24.1	181.2 / −72.6	175.4 / −45.9
	0.005	170.8 / 83.7	168.5 / 25.0	181.3 / −69.8	175.6 / −49.5
	0.03	170.1 / 64.9	168.7 / 41.5	179.7 / −45.6	175.9 / −69.8
	0.03	171.6 / 67.1	168.7 / 39.6	179.9 / −45.7	176.3 / −71.0
	1.0	172.1 / 69.2	168.9 / 40.5	180.1 / −43.9	176.5 / −74.4
	1.0	171.6 / 68.8	169.1 / 35.9	180.0 / −45.4	176.2 / −68.2
	mean	171.3 ± 0.7 73.3 ± 8.3	168.8 ± 0.2 34.4 ± 7.2	180.3 ± 0.6 -53.8 ± 12.3	175.9 ± 0.4 -63.1 ± 11.1

Table S2 The experimental data on the phase transition temperatures (K) / enthalpies (J/g) for TFAAA solutions in cyclohexane. T_{fC} – fusion temperature, T_{cC} — crystallization temperature, $T_{I/II}$ -– temperature of I→II phase transition, and $T_{II/I}$ — temperature of II→I phase transition. $T'_{I/II}$ and $T'_{II/I}$ – denote the position of the satellite peaks below the I↔II transition temperature (T_2).

	C, mg/ml	T_{cC}	T_{fC}	$T_{I/II}$	$T'_{I/II}$	$T_{II/I}$	$T'_{II/I}$
Cyclohexane		276.8 ± 0.9 28.5 ± 2.1	279.8 ± 0.5 -28.6 ± 1.6	180.0 ± 0.5 64.9 ± 1.4	–	187.7 ± 0.7 -70.4 ± 0.9	–
TFAAA-4	0.20	275.3 / 29.2	278.1 / −28.0,	181.4 / 73.8	167.5 / 0.5	188.2 / −80.5	174.3 / −0.4
	1.0	273.7 / 24.1	277.7 / −22.5	181.0 / 65.2	167.8 / 2.2	188.1 / −70.8	174.3 / −1.6
	2.0	261.6 / 11.7	268.8 / −1.7	181.7 / 47.1	169.5 / 6.1	188.1 / −57.6	175.2 / −7.3
	mean	270.2 ± 6.1 12.7 ± 7.3	274.9 ± 4.3 -17.4 ± 11.3	181.3 ± 0.3 62.0 ± 11.1	168.2 ± 0.9 2.9 ± 2.3	188.1 ± 0.0 -69.6 ± 9.4	174.5 ± 0.4 -3.1 ± 3.0
TFAAA-5	0.10	244.1 / 5.4	253.7 / −0.7	178.4 / 52.8	169.4 / 18.2	188.0 / −50.3	175.6 / −20.6
	0.5	276.3 / 31.9	279.2 / −32.6	181.7 / 54.6	169.5 / 7.6	188.2 / −67.2	175.2 / −8.7
	1.0	264.3 / 11.0	267.3 / −2.1	181.6 / 53.1	169.7 / 8.4	188.3 / −65.0	175.3 / −9.4
	mean	257.8 ± 9.8 9.2 ± 2.7	266.7 ± 10.4 -11.8 ± 14.7	180.5 ± 1.5 53.5 ± 0.8	169.5 ± 0.1 11.4 ± 4.8	188.1 ± 0.1 -60.9 ± 7.5	175.3 ± 0.2 -12.9 ± 5.5
TFAAA-6	0.20	260.6 / 12.2	265.7 / −1.6	181.3 / 53.2	169.7 / 9.0	188.3 / −64.3	175.2 / −10.4
	1.0	262.8 / 11.4	267.0 / −1.7	181.5 / 54.0	169.7 / 7.9	188.1 / −66.4	175.1 / −9.2
	2.0	263.8 / 13.1	267.9 / −1.9	181.4 / 54.2	169.7 / 6.9	188.3 / −65.4	175.2 / −8.1
	mean	262.5 ± 1.3 12.2 ± 0.7	267.0 ± 0.9 -1.8 ± 0.1	181.6 ± 0.1 53.8 ± 0.4	169.7 ± 0.0 7.9 ± 0.9	188.4 ± 0.1 -65.3 ± 0.9	175.3 ± 0.0 -9.2 ± 0.9
TFAAA-7	0.005	259.2 / 12.3	266.1 / −2.3	182.1 / 57.9	169.7 / 9.8	188.2 / −71.2	175.4 / −10.9
	0.005	260.6 / 12.9	266.8 / −2.1	181.9 / 58.8	169.6 / 8.9	188.2 / −71.7	175.2 / −10.3
	0.03	262.5 / 11.6	267.8 / −1.8	181.5 / 52.7	170.1 / 7.3	188.6 / −64.5	175.4 / −8.9
	1.0	260.8 / 9.6	263.9 / −1.3	181.4 / 54.2	170.1 / 11.2	188.2 / −65.4	175.4 / −12.5
	mean	260.7 ± 1.2 11.6 ± 1.2	266.1 ± 1.4 -1.9 ± 0.4	181.7 ± 0.3 55.9 ± 2.5	169.8 ± 0.2 9.3 ± 1.4	188.2 ± 0.2 -68.2 ± 3.3	175.3 ± 0.1 -10.7 ± 1.3

Table S3 The Raoult's law estimates on the e"raoult's" TFAAA concentrations (C_{eff} mg/ml) and Gibbs-Thompson's estimates on the mesophase (D_m, μm) and strings (D_s, nm) diameters in heptane and cyclohexane solutions. The last column represents the average spacing between the strings (S_s μm).

	C, mg/ml	Heptane				Cyclohexane			
	(real)	C_{eff}	D_m	D_s	S_s	C_{eff}	D_m	D_s	S_s
TFAAA-4	0.10	690	0.72	55	31				
	0.10	690	0.67	50	28			–	
	0.20			–		8	3.5	740	260
	0.40	520	1.2	100	27				
	0.40	520	1.1	100	26			–	
	1.0	530	1.2	235	24				
	1.0	550	1.2	230	23	20	3.7	710	125
	2.0			–		115	4.0	720	72
	mean	580 ± 30	1.0 ± 0.2	130 ± 80	26.3 ± 2.5	45 ± 45	3.7 ± 0.2	720 ± 10	151 ± 79
TFAAA-5	0.05	480	0.98	37	29				
	0.05	470	1.1	42	32			–	
	0.10			–		205	5.5	120	66
	0.20	590	0.67	84	32				
	0.20	580	0.72	92	36			–	
	0.50			–		70	4.0	285	70
	1.0	495	0.75	135	24	75	4.1	550	68
	1.0	495	0.77	140	24				
	mean	520 ± 50	0.83 ± 0.15	90 ± 40	29.7 ± 4.1	120 ± 60	4.53 ± 0.07	320 ± 180	68.1 ± 1.7
TFAAA-6	0.05	505	1.0	39	30				
	0.05	505	1.1	38	30			–	
	0.20	490	1.0	80	31	105	4.2	173	67
	0.20	500	1.1	77	30				
	1.0	490	0.95	204	25	90	4.1	404	70
	1.0	485	0.96	205	25				
	2.0			–		85	4.1	607	74
	mean	496 ± 8	1.02 ± 0.06	105 ± 70	29.0 ± 2.5	93 ± 8	4.17 ± 0.05	395 ± 175	70.6 ± 3.1
TFAAA-7	0.005	580	2.2	10	28	155	3.9	29	64
	0.005	620	2.7	13	35	145	4.0	30	67
	0.03	605	2.5	24	44	125	4.3	76	76
	0.03	605	2.2	23	22				
	1.0	590	1.9	114	20	140	4.4	370	64
	1.0	570	2.5	151	26				
	mean	595 ± 15	2.6 ± 0.3	55 ± 55	29.1 ± 8.2	140 ± 10	4.2 ± 0.2	125 ± 140	67.9 ± 4.8