Solute-Solvent Interactions in Lactams/Water Ternary Solvents

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ELECTRONIC SUPPLEMENTARY INFORMATION

Table S1 Literature and this work values of the thermophysical properties of pure solvents at 298.15 K.

Property	PYR	NMP	W
Density / g cm^{-3}	1.10747 [a] 1.10747 [b] 1.10712 [c] 1.10722 [d]	1.02788 [a] 1.02832 [b] 1.0262 [e] 1.0286 [f] 1.0259 [g]	0.99704 [a] 0.9970474 [g] 0.9970480 [h]
Dynamic Viscosity / mPa s	13.39 [a] 13.1 [b] 13.3 [i]	1.727 [a] 1.66 [b] 1.667 [f] 1.666 [g]	0.890 [a] 0.89025 [g] 0.89008 [j]
Speed of Sound / m s^{-1}	1633.4 [a]	1545.0 [a]	1497.0 [a] 1497.4 [h] 1496.7 [j]
Refractive Index	1.48649 [a] 1.486 [g]	1.46876 [a] 1.4675 [g] 1.4675 [k]	1.33250 [a] 1.3325019 [g]
Isentropic Compresibility / TPa^{-1}	338.44 [a]	407.55 [a]	447.54 [a]
Internal Pressure / MPa	119.21 [a]	92.37 [a]	394.45 [a]
Isobaric Molar Heat Capacity / J mol^{-1} K^{-1}	160.28 [a]	174.39 [a]	76.07 [a] 75.328 [j]

[a] This work. [b] Ref. 12. [c] Ref. 13. [d] Ref. 14. [e] Ref. 9. [f] Ref. 15. [g] Ref. 16. [h] Ref. 17. [i] Ref. 18. [j] Ref. 19. [k] Ref. 7.

Table S2 Experimental densities, $\rho/\mathrm{g\,cm^{-3}}$, dynamic viscosities, $\eta/\mathrm{mPa\,s}$, speeds of sound, $u/\mathrm{m\,s^{-1}}$, refractive indices, n_D, isentropic compressibilities, $k_S/\mathrm{TPa^{-1}}$, and internal pressures, P_i/MPa, of the *x* PYR + (1 – *x*)W, *x* NMP + (1 – *x*) W and *x* PYR + (1 – *x*) NMP binary mixtures at 298.15 K.

x	ρ	η	u	n_D	k_S	P_i
			x PYR + (1 – *x*)W			
0.0502	1.02139	1.470	1599.9		382.49	
0.1007	1.04146	2.240	1665.2	1.38579	346.27	327.60
0.1507	1.05692	3.170	1704.6		325.62	
0.2024	1.06916	4.250	1726.8	1.41786	313.69	277.88
0.2554	1.07855	5.430	1736.1		307.63	
0.3052	1.08520	6.530	1736.8	1.44335	305.48	241.21
0.3570	1.09039	7.600	1732.6		305.50	
0.4091	1.09429	8.580	1725.5	1.45586	306.94	210.08
0.4579	1.09712	9.390	1717.3		309.08	
0.5088	1.09935	10.110	1708.7	1.46501	311.55	186.67
0.5569	1.10109	10.690	1699.9		314.30	
0.6156	1.10270	11.280	1689.4	1.47339	317.76	166.82
0.6612	1.10369	11.650	1681.2		320.55	
0.7216	1.10475	12.080	1671.2	1.47805	324.09	150.34
0.7662	1.10536	12.340	1664.3		326.61	
0.8231	1.10604	12.620	1656.1	1.48126	329.66	137.21
0.8637	1.10645	12.820	1650.2		331.91	
0.9327	1.10703	13.130	1641.5	1.48462	335.25	125.47
0.9662	1.10730	13.284	1637.4		336.85	
			x NMP + (1 – *x*) W			
0.0505	1.01275	1.861	1631.0		371.17	
0.1007	1.02639	2.898	1705.0	1.38937	335.16	307.31
0.1517	1.03650	3.978	1741.3		318.18	
0.2008	1.04160	4.791	1750.8	1.42150	313.21	250.80
0.2518	1.04584	5.189	1746.3		313.55	
0.3010	1.04726	5.215	1733.2	1.43921	317.87	209.74
0.3515	1.04725	4.998	1716.7		324.03	
0.4035	1.04632	4.736	1698.2	1.44976	331.42	178.20
0.4551	1.04496	4.256	1679.7		339.19	
0.5017	1.04351	3.892	1664.5	1.45714	345.87	155.44
0.5499	1.04172	3.497	1647.9		353.52	
0.6022	1.03954			1.46040		136.67
0.6499	1.03808	2.857	1618.1		367.92	
0.7014	1.03626	2.596	1604.4	1.46326	374.90	122.16
0.7515	1.03445	2.359	1590.9		381.95	
0.8028	1.03296	2.198	1580.5	1.46584	387.55	110.17
0.8507	1.03158	2.062	1570.8		392.88	
0.9034	1.03014	1.929	1560.8	1.46722	398.51	100.27
0.9502	1.02898	1.833	1552.9		403.02	
			x PYR + (1 – *x*) NMP			
0.0499	1.03159	1.857	1551.0		402.98	
0.1004	1.03534	2.017	1556.6	1.47068	398.61	94.66
0.1498	1.03903	2.185	1561.9		394.52	
0.1993	1.04274	2.371	1567.1	1.47263	390.52	97.01
0.2495	1.04652	2.583	1572.0		386.65	
0.3001	1.05037	2.821	1577.0	1.47456	382.82	99.48
0.3497	1.05416	3.080	1581.7		379.20	
0.3986	1.05796	3.373	1586.1	1.47627	375.72	101.95
0.4492	1.06190	3.715	1590.7		372.16	
0.4994	1.06583	4.101	1595.2	1.47809	368.73	104.59
0.5493	1.06979	4.539	1599.6		365.31	
0.5989	1.07376	5.030	1603.8	1.47981	362.08	107.28
0.6497	1.07787	5.615	1607.9		358.86	
0.6992	1.08193	6.269	1611.9	1.48151	355.76	110.09
0.7487	1.08602	7.022	1615.7		352.72	
0.7986	1.09019	7.918	1619.8	1.48317	349.59	112.99
0.8494	1.09446	8.969	1623.2		346.76	
0.9011	1.09883	10.232	1627.5	1.48486	343.57	116.09
0.9503	1.10307	11.651	1630.5		340.99	

Table S3 Experimental isobaric molar heat capacities, $C_{P,m}$ / J mol^{-1}K^{-1}, of the x PYR + (1 – x)W, x NMP + (1 – x) W and x PYR + (1 – x) NMP binary mixtures at 298.15 K.

x PYR + (1 - x) W		x NMP + (1 - x) W		x PYR + (1 - x) NMP	
x	$C_{P,m}$	x	$C_{P,m}$	x	$C_{P,m}$
0.0478	83.17	0.0307	82.13	0.0503	173.78
0.0960	89.40	0.0518	86.26	0.0707	173.57
0.1480	95.58	0.0847	91.87	0.1006	173.22
0.2467	105.10	0.1537	101.89	0.1487	172.60
0.3455	113.86	0.2039	107.97	0.1997	171.95
0.4485	122.04	0.2602	114.26	0.3003	170.57
0.5457	129.05	0.3094	118.92	0.3515	169.87
0.6446	135.94	0.3622	123.77	0.5009	167.77
0.7471	142.99	0.4648	131.99	0.6042	166.31
0.8524	150.40	0.5541	139.52	0.7556	164.10
0.9485	157.10	0.6265	144.99	0.8338	162.94
		0.7451	154.11	0.8989	161.91
		0.8582	162.88		

Table S4 Experimental densities, $\rho/\mathrm{g\ cm^{-3}}$, dynamic viscosities, $\eta/\mathrm{mPa\ s}$, speeds of sound, $u/\mathrm{m\ s^{-1}}$, refractive indices, n_D, isentropic compressibilities, $k_S/\mathrm{TPa^{-1}}$, and internal pressures, P_i/MPa, of the x_1 PYR + x_2 NMP + $(1-x_1-x_2)$ W ternary mixtures at 298.15 K.

x_1	x_2	ρ	η	u	n_D	k_S	P_i
0.0905	0.8107	1.03744	2.265	1573.9	1.46897	389.12	102.89
0.0805	0.7228	1.03976	2.546	1590.8	1.46722	380.05	112.61
0.0698	0.6317	1.04258	2.980	1613.1	1.46470	368.60	124.82
0.0600	0.5422	1.04571	3.560	1640.9	1.46165	355.15	139.54
0.0500	0.4537	1.04856	4.283	1669.2	1.45689	342.30	157.58
0.0398	0.3615	1.05085	5.077	1703.5	1.44995	327.94	181.71
0.0300	0.2708	1.05076	5.479	1736.0	1.35493	315.81	185.28
0.0201	0.1806	1.04515	4.786	1750.0	1.34845	312.43	225.09
0.1797	0.7207	1.04466	2.658	1584.5	1.47075	381.30	105.44
0.1598	0.6417	1.04660	2.986	1600.1	1.46870	373.21	115.40
0.1402	0.5653	1.04887	3.425	1620.6	1.46611	363.03	126.98
0.1212	0.4825	1.05160	4.047	1646.4	1.46258	350.82	142.11
0.0983	0.4017	1.05382	4.763	1676.3	1.45736	337.69	161.21
0.0803	0.3217	1.05544	5.477	1708.6	1.44967	324.56	184.31
0.0609	0.2414	1.05443	5.651	1738.7	1.43795	313.73	214.64
0.0198	0.0806	1.02923	2.822	1698.8	1.38650	336.69	310.39
0.2694	0.6316	1.05140	4.746	1589.0	1.42202	376.68	99.54
0.2411	0.5638	1.05349	5.850	1608.2		367.01	
0.2105	0.4930	1.05548	5.845	1629.2	1.45079	356.96	126.69
0.1831	0.4302	1.05729	5.285	1650.9	1.45829	347.05	142.10
0.1492	0.3517	1.05924	4.516	1681.8	1.46411	333.76	165.64
0.1195	0.2818	1.05990	3.969	1711.8	1.46743	321.98	192.75
0.0901	0.2113	1.05778	3.472	1739.7	1.47036	312.35	229.38
0.0592	0.1410	1.04962	3.027	1746.9	1.47286	312.21	281.68
0.3591	0.5424	1.06017	3.689	1607.4	1.47425	365.05	110.65
0.3208	0.4826	1.06055	4.095	1616.8	1.47170	360.71	120.64
0.2820	0.4217	1.06220	4.615	1636.7	1.46871	351.44	133.01
0.2409	0.3634	1.06357	5.259	1659.6	1.46464	341.35	147.87
0.2008	0.3018	1.06478	5.878	1688.3	1.45862	329.50	166.81
0.1601	0.2411	1.06460	6.255	1715.2	1.45099	319.29	190.88
0.1200	0.1812	1.06156	6.019	1740.1	1.43870	311.12	221.17
0.0397	0.0601	1.03192	2.706	1690.6	1.34299	339.06	293.07
0.4504	0.4504	1.06675	4.459	1609.4	1.47573	361.91	113.34
0.4000	0.4030	1.06771					
0.3511	0.3518	1.06886	5.376	1644.2	1.47249	346.08	136.63
0.3023	0.3041	1.06979	5.917	1666.7	1.46562	336.51	150.63
0.2501	0.2509	1.07023	6.543	1692.4	1.45948	326.25	170.37
0.2005	0.2003	1.06919	6.664	1720.0	1.45064	316.17	193.99
0.1504	0.1509	1.06528	6.176	1740.7	1.43870	309.81	224.27
0.1005	0.0998	1.05443	4.660	1742.1	1.41878	312.50	264.05
0.5434	0.3637	1.07431	5.385	1616.3	1.47697	356.33	115.46
0.4853	0.3246	1.07577	5.784	1653.2	1.47464	340.12	125.77
0.4236	0.2830	1.07614	6.325	1670.2	1.47032	333.11	138.50
0.3680	0.2452	1.07585	6.711	1696.0	1.46701	323.15	152.71
0.3016	0.2016	1.07500	7.096	1721.9	1.46059	313.73	173.15
0.2398	0.1607	1.06916	7.046	1741.3	1.45172	308.47	196.69
0.0589	0.0399	1.03370	2.549	1680.2	1.38620	342.68	319.98
0.6350	0.2737	1.08214	5.385	1623.9	1.47883	350.43	118.27
0.5710	0.2467	1.08236	5.784	1637.3	1.47314	344.63	127.19
0.4899	0.2109	1.08265	6.325	1660.2	1.47015	335.10	142.17
0.4321	0.1860	1.08252	6.711	1674.5	1.46803	329.46	155.13
0.3523	0.1515	1.08152	7.096	1699.9	1.46112	319.99	176.49
0.2803	0.1196	1.07888	7.046	1723.6	1.45189	312.02	201.15

Table S4 Continued.

x_1	x_2	ρ	η	u	n_D	k_S	P_i
0.2119	0.0912	1.07266	6.281	1740.9	1.43871	307.61	229.90
0.1397	0.0601	1.06026	2.549	1736.9	1.41891	312.65	270.43
0.7255	0.1819	1.09017	8.133	1632.5	1.48063	344.19	121.50
0.6528	0.1637	1.09014	8.361	1643.6	1.47771	339.58	131.17
0.5732	0.1446	1.08981	8.582	1659.9	1.47382	333.04	143.50
0.5001	0.1252	1.08930	8.745	1679.0	1.46934	325.67	157.37
0.4259	0.1049	1.08811	8.649	1697.6	1.46354	318.91	174.50
0.3225	0.0804	1.08391	7.858	1724.5	1.45251	310.23	203.84
0.2404	0.0603	1.07620	6.387	1740.5	1.43792	306.73	233.89
0.8215	0.0852	1.09893	10.395	1639.6	1.48208	338.51	124.92
0.7449	0.0745	1.09872	10.449	1650.7	1.47919	334.01	134.41
0.6561	0.0654	1.09799	10.383	1665.8	1.47520	328.22	146.75
0.5435	0.0562	1.09604	9.969	1687.8	1.46849	320.27	165.33
0.4499	0.0507	1.09313	9.287	1706.7	1.46164	314.07	184.09
0.3618	0.0358	1.08908	8.181	1726.5	1.45169	308.05	208.99
0.2720	0.0270	1.08076	6.440	1739.0	1.43770	305.97	238.36
0.1797	0.0186	1.06573	4.351	1729.8	1.41802	313.59	277.26
0.0900	0.0094	1.03953	2.344	1668.8	1.38497	345.42	326.15

Table S5 Experimental isobaric molar heat capacities, $C_{P,m}$ / J mol^{-1}K^{-1}, of the x_1 PYR + x_2 NMP + (1 – x_1 – x_2) W ternary mixtures at 298.15 K.

x_1	x_2	$C_{P,m}$	x_1	x_2	$C_{P,m}$	x_1	x_2	$C_{P,m}$
0.0905	0.8086	166.93	0.3334	0.4584	154.57	0.5007	0.1938	143.79
0.0801	0.7212	159.30	0.2806	0.4191	148.15	0.4200	0.1812	137.52
0.0715	0.6284	151.25	0.2412	0.3551	140.87	0.3543	0.1515	130.53
0.0608	0.5419	144.30	0.2009	0.2993	133.59	0.2797	0.1206	122.61
0.0503	0.4529	136.66	0.1615	0.2431	126.19	0.2090	0.0914	114.32
0.0410	0.3461	127.30	0.1162	0.1815	117.01	0.1402	0.0600	104.69
0.0296	0.2719	119.24	0.0396	0.0595	94.21	0.7173	0.1840	157.13
0.0197	0.1852	109.48	0.4465	0.4527	161.90	0.6408	0.1615	150.30
0.1752	0.7252	165.26	0.3998	0.4003	154.53	0.5575	0.1442	144.72
0.1605	0.6404	157.61	0.3504	0.3530	147.83	0.4832	0.1195	137.81
0.1401	0.5652	150.50	0.3016	0.3024	140.62	0.3978	0.1009	130.32
0.1183	0.4847	143.15	0.2498	0.2520	133.11	0.3234	0.0809	122.36
0.1026	0.3879	134.58	0.2014	0.2012	125.28	0.2412	0.0608	113.09
0.0798	0.3237	128.72	0.1498	0.1515	116.20	0.8093	0.0918	157.31
0.0613	0.2423	119.35	0.0994	0.0990	105.27	0.7212	0.0801	149.81
0.0199	0.0811	95.97	0.5409	0.3610	160.48	0.6322	0.0679	142.70
0.2697	0.6318	165.93	0.4824	0.3204	153.14	0.5415	0.0606	135.28
0.2424	0.5613	158.37	0.4212	0.2788	145.78	0.4496	0.0510	127.99
0.2117	0.4886	150.58	0.3596	0.2430	139.03	0.3535	0.0406	120.16
0.1803	0.4207	142.40	0.3152	0.1881	131.43	0.2695	0.0300	112.34
0.1584	0.3660	136.57	0.2410	0.1586	123.58	0.1789	0.0202	103.51
0.1216	0.2795	126.88	0.1794	0.1208	115.20	0.0882	0.0101	91.47
0.0908	0.2106	118.30	0.0601	0.0401	93.53			
0.0608	0.1323	106.89	0.6302	0.2690	158.29			
0.3640	0.5381	162.82	0.5641	0.2387	151.57			

Table S6 Coordinates for the maxima and minima of the ternary contributions to the different excess and mixing properties defined according to eqn. (2) for the x_1 PYR + x_2 NMP + (1 – x_1 – x_2) W Ternary System at 298.15 K.

	Maximum		*Minimum*	
Property	*Position*	*Amount*	*Position*	*Amount*
$\left(V^E_{m,TER} - V^E_{m,BIN}\right)/\mathrm{cm^3mol^{-1}}$	x_1 = 0.2909 x_2 = 0.3076	0.0964	—	—
$\left(\Delta_{mix}\eta_{TER} - \Delta_{mix}\eta_{BIN}\right)/\mathrm{mPa\ s}$	x_1 = 0.0729 x_2 = 0.4859	0.118	x_1 = 0.5465 x_2 = 0.2256	-0.960
$\left(\Delta G^{*E}_{m,TER} - \Delta G^{*E}_{m,BIN}\right)/\mathrm{kJ\ mol^{-1}}$	x_1 = 0.1680 x_2 = 0.7189	0.134	x_1 = 0.3117 x_2 = 0.1977	-0.729
$\left(k^E_{S,TER} - k^E_{S,BIN}\right)/\mathrm{TPa^{-1}}$	x_1 = 0.2234 x_2 = 0.6493	3.40	x_1 = 0.2679 x_2 = 0.1857	-8.89
$\left(P^E_{i,TER} - P^E_{i,BIN}\right)/\mathrm{MPa}$	x_1 = 0.2731 x_2 = 0.2587	10.35	—	—
$\left(C^E_{P,m,TER} - C^E_{P,m,BIN}\right)/\mathrm{Jmol^{-1}K^{-1}}$	x_1 = 0.3226 x_2 = 0.4014	1.47	—	—

Table S7 Coordinates for the maxima and minima of the partial molar excess properties, and values at infinite dilution for the binary constituents at 298.15 K.

Compound	*Minimum*		*Maximum*		*Value at infinite dilution*	Minimum		Maximum		*Value at infinite dilution*
	Position	*Amount*	*Position*	*Amount*		*Position*	*Amount*	*Position*	*Amount*	
	x PYR + (1 - x) W									
	$\overline{V}^E$ / $cm^3 mol^{-1}$					$\overline{C}^E_{p,m}$ / J $mol^{-1} K^{-1}$				
PYR	0.0963	-2.23	0.9301	0.00	-1.44	0.6604	0.00	0.8473	0.62	78.37
W	0.9301	-1.38	0.0963	0.03	-1.38	0.8463	13.76	0.6604	15.71	27.41
	x NMP + (1 - x) W									
	$\overline{V}^E$ / $cm^3 mol^{-1}$					$\overline{C}^E_{p,m}$ / J $mol^{-1} K^{-1}$				
NMP	0.0882	-4.83	0.9018	0.01	-3.40	0.5546	-1.07	0.8327	0.37	108.56
W	0.9018	-2.67	0.0882	0.04	-2.21	0.8327	17.39	0.5546	20.65	24.16
	x PYR + (1 - x) NMP									
	$\overline{V}^E$ / $cm^3 mol^{-1}$					$\overline{C}^E_{p,m}$ / J $mol^{-1} K^{-1}$				
PYR	–––	–––	–––	–––	-1.04	–––	–––	–––	–––	3.04
NMP	–––	–––	–––	–––	-0.78	–––	–––	–––	–––	2.74