



SUPPLEMENTARY MATERIAL

**Ionic-interaction of aqueous and alcoholic poly(vinyl alcohol)  
in the presence of protons**

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TABLE S-I. Densities of poly(vinyl alcohol)-solvent systems in acetic acid at different temperatures

[CH <sub>3</sub> COOH] (mol dm <sup>-3</sup> )	Densities x10 <sup>3</sup> (kg/m <sup>3</sup> )				
	Temperature (K)				
	305	308	313	318	323
0.1% (w/v) PVOH in water					
0.1	0.9887	0.9877	0.9861	0.9848	0.9830
0.2	0.9894	0.9886	0.9871	0.9856	0.9836
0.3	0.9901	0.9893	0.9879	0.9860	0.9838
0.4	0.9908	0.9900	0.9880	0.9869	0.9845
0.5	0.9914	0.9906	0.9891	0.9878	0.9854
0.5% (w/v) PVOH in water					
0.1	0.9895	0.9892	0.9876	0.9858	0.9846
0.2	0.9905	0.9893	0.9879	0.9864	0.9848
0.3	0.9912	0.9902	0.9882	0.9868	0.9850
0.4	0.9915	0.9907	0.9887	0.9871	0.9851
0.5	0.9925	0.9911	0.9895	0.9877	0.9856
0.1% (w/v) PVOH in 5% (v/v) methanol					
0.1	0.9829	0.9823	0.9808	0.9788	0.9779
0.2	0.9834	0.9829	0.9813	0.9801	0.9789
0.3	0.9851	0.9846	0.9830	0.9810	0.9803
0.4	0.9865	0.9853	0.9838	0.9821	0.9811
0.5	0.9879	0.9867	0.9853	0.9837	0.9822
0.5% (w/v) PVOH in 5% (v/v) methanol					
0.1	0.9835	0.9827	0.9819	0.9806	0.9793
0.2	0.9846	0.9842	0.9833	0.9819	0.9799
0.3	0.9859	0.9854	0.9838	0.9828	0.9818
0.4	0.9876	0.9866	0.9851	0.9841	0.9817
0.5	0.9886	0.9877	0.9867	0.9855	0.9841

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TABLE S-I. Continued

[CH <sub>3</sub> COOH] (mol dm <sup>-3</sup> )	Densities × 10 <sup>3</sup> (kg/m <sup>3</sup> )				
	Temperature (K)				
	305	308	313	318	323
0.1% (w/v) PVOH in 5% (v/v) ethanol					
0.1	0.9824	0.9822	0.9804	0.9775	0.9769
0.2	0.9830	0.9828	0.9809	0.9790	0.9784
0.3	0.9845	0.9841	0.9925	0.9801	0.9795
0.4	0.9854	0.9853	0.9831	0.9914	0.9799
0.5	0.9870	0.9863	0.9848	0.9823	0.9814
0.5% (w/v) PVOH in 5% (v/v) ethanol					
0.1	0.9829	0.9826	0.9811	0.9801	0.9787
0.2	0.9837	0.9835	0.9822	0.9810	0.9790
0.3	0.9851	0.9848	0.9832	0.9823	0.9801
0.4	0.9863	0.9860	0.9844	0.9837	0.9811
0.5	0.9881	0.9873	0.9852	0.9846	0.9831
0.1% (w/v) PVOH in 5% (v/v) 2-propanol					
0.1	0.9826	0.9822	0.9806	0.9780	0.9775
0.2	0.9832	0.9830	0.9810	0.9797	0.9787
0.3	0.9849	0.9845	0.9828	0.9805	0.9800
0.4	0.9856	0.9853	0.9835	0.9919	0.9808
0.5	0.9874	0.9865	0.9850	0.9829	0.9820
0.5% (w/v) PVOH in 5% (v/v) 2-propanol					
0.1	0.9831	0.9826	0.9817	0.9804	0.9791
0.2	0.9839	0.9837	0.9828	0.9817	0.9797
0.3	0.9857	0.9854	0.9835	0.9825	0.9803
0.4	0.9867	0.9863	0.9845	0.9839	0.9815
0.5	0.9884	0.9876	0.9859	0.9848	0.9839
0.1% (w/v) PVOH in 5% (v/v) 1-butanol					
0.1	0.9832	0.9825	0.9812	0.9790	0.9781
0.2	0.9840	0.9834	0.9818	0.9803	0.9792
0.3	0.9855	0.9851	0.9831	0.9816	0.9806
0.4	0.9869	0.9856	0.9844	0.9825	0.9813
0.5	0.9882	0.9869	0.9860	0.9841	0.9829
0.5% (w/v) PVOH in 5% (v/v) 1-butanol					
0.1	0.9837	0.9829	0.9821	0.9809	0.9798
0.2	0.9849	0.9844	0.9837	0.9821	0.9803
0.3	0.9863	0.9858	0.9844	0.9830	0.9813
0.4	0.9878	0.9869	0.9853	0.9845	0.9819
0.5	0.9889	0.9877	0.9870	0.9858	0.9845

Mean ± standard deviation = 0.9842 ± 0.00327

TABLE S-II. Viscosities of poly(vinyl alcohol)-solvent systems in acetic acid different temperatures

[CH <sub>3</sub> COOH] (mol dm <sup>-3</sup> )	Viscosity x10 <sup>4</sup> (Pa. s)				
	Temperature (K)				
	305	308	313	318	323
0.1% (w/v) PVOH in water					
0.1	8.4955	7.6506	6.9522	6.3164	5.7911
0.2	8.4203	7.6073	6.8946	6.2775	5.7736
0.3	8.3450	7.5625	6.8766	6.2359	5.7537
0.4	8.3238	7.4924	6.7886	6.2196	5.7367
0.5	8.2203	7.4215	6.7705	6.2032	5.7208
0.5% (w/v) PVOH in water					
0.1	11.346	9.8729	8.8521	7.9971	7.4247
0.2	11.194	9.3966	8.6899	7.9579	7.2915
0.3	10.660	9.3548	8.4099	7.6965	7.1323
0.4	10.175	8.7773	8.0606	7.3238	6.8165
0.5	9.9133	8.6793	7.7369	7.0634	6.7988
0.1% (w/v) PVOH in 5% (v/v) methanol					
0.1	8.8975	8.1035	7.3649	6.4649	6.0335
0.2	8.7459	7.9636	7.1867	6.4218	6.0186
0.3	8.6307	7.9290	7.1493	6.3733	6.0081
0.4	8.5576	7.7821	7.1295	6.3239	5.9919
0.5	8.4616	7.7430	7.0934	6.2945	5.9758
0.5% (w/v) PVOH in 5% (v/v) methanol					
0.1	11.735	10.107	9.1241	8.2154	7.5208
0.2	11.257	9.8290	9.0884	7.9622	7.3473
0.3	10.697	9.4095	8.6304	7.7051	7.2316
0.4	10.377	9.1472	8.3600	7.4015	7.0243
0.5	10.036	8.9047	8.0560	7.2220	6.8848
0.1% (w/v) PVOH in 5% (v/v) ethanol					
0.1	9.0551	8.1259	7.4021	6.5629	6.1528
0.2	8.8573	8.0618	7.2488	6.4621	6.0784
0.3	8.7602	7.9975	7.2109	6.4248	6.0642
0.4	8.6360	7.9322	7.2006	6.4323	6.0500
0.5	8.5680	7.7939	7.1375	6.3086	6.0129
0.5% (w/v) PVOH in 5% (v/v) ethanol					
0.1	11.844	10.477	9.3657	8.3232	7.5689
0.2	11.452	10.215	9.1315	8.0458	7.4873
0.3	10.711	9.7289	8.8361	7.7752	7.3017
0.4	10.465	9.3401	8.3837	7.4744	6.9148
0.5	10.225	9.0515	8.2048	7.4175	6.9005

TABLE S-II. Continued

[CH <sub>3</sub> COOH] (mol dm <sup>-3</sup> )	Viscosity x10 <sup>4</sup> (Pa. s)				
	Temperature (K)				
	305	308	313	318	323
0.1% (w/v) PVOH in 5% (v/v) 2-propanol					
0.1	9.4933	8.4624	7.4314	6.7819	6.2183
0.2	8.9658	8.1134	7.3256	6.5601	6.1431
0.3	8.8806	8.0622	7.2812	6.5664	6.1045
0.4	8.7790	7.9491	7.2497	6.5525	6.0804
0.5	8.6734	7.8950	7.2123	6.4451	6.0496
0.5% (w/v) PVOH in 5% (v/v) 2-propanol					
0.1	12.528	10.908	9.5013	8.6505	7.8983
0.2	11.956	10.642	9.3713	8.2181	7.5188
0.3	11.486	10.105	9.0263	8.0223	7.3712
0.4	10.557	9.5684	8.4600	7.6364	7.1063
0.5	10.442	9.1295	8.2493	7.5047	7.0135
0.1% (w/v) PVOH in 5% (v/v) 1-butanol					
0.1	9.6291	8.5282	7.7188	7.0517	6.2613
0.2	9.3975	8.2666	7.5597	6.8168	6.1624
0.3	9.1422	8.1258	7.4056	6.7814	6.1066
0.4	8.9931	8.0340	7.2746	6.7432	6.0913
0.5	8.8968	7.9451	7.1689	6.6649	6.0789
0.5% (w/v) PVOH in 5% (v/v) 1-butanol					
0.1	12.867	11.059	9.9622	8.9643	7.9196
0.2	12.202	10.770	9.5972	8.3088	7.6606
0.3	11.673	10.298	9.2262	8.1265	7.4743
0.4	11.144	9.7108	8.5635	7.6786	7.1076
0.5	10.667	9.4904	8.3123	7.5473	7.0783

Mean ± standard deviation = 8.1199 ± 1.5247

TABLE S-III. The pH of the acetic acid solution in different percentage composition (w/v) of aqueous and 5% (v/v) alcoholic poly(vinyl alcohol)

[CH <sub>3</sub> COOH] (mol dm <sup>-3</sup> )	pH				
	water	5% (v/v)	5% (w/v)	5% (w/v)	5% (w/v)
		methanol	ethanol	2-propanol	1-butanol
0.1% (w/v) PVOH					
0.1	3.12	3.12	3.10	3.10	3.10
0.5	2.80	2.82	2.80	2.76	2.80
0.5% (w/v) PVOH					
0.1	3.76	3.58	3.50	3.46	3.24
0.5	3.16	2.88	2.86	2.86	2.84

TABLE S-IV. *A*-coefficient and *B*-coefficient of acetic acid in % (w/v) composition of PVOH-water system at different temperatures

Temperature (K)	Ion-Ion interaction (A-coefficient) ( $\text{mol}^{-1} \text{dm}^3$ ) <sup>1/2</sup>		
	0.10% (w/v) PVOH	0.35% (w/v) PVOH	0.50% (w/v) PVOH
Water			
305	0.3198	1.1522	2.0952
308	0.3155	1.1473	1.7954
313	0.3146	1.1261	1.7721
318	0.2806	0.9920	1.7204
323	0.2732	0.9734	1.7155
Ion-Solvent interaction (B-coefficient) ( $\text{mol}^{-1} \text{dm}^3$ )			
305	-0.4038	-1.4190	-2.5814
308	-0.3940	-1.3677	-2.2357
313	-0.3888	-1.3666	-2.2020
318	-0.3334	-1.3599	-2.1136
323	-0.3077	-1.0957	-2.0412

TABLE S-V. A-coefficient and B-coefficient of acetic acid in % (w/v) composition of the alcoholic-PVOH system at different temperatures

Temperature (K)	Ion-Ion interaction (A-coefficient) ( $\text{mol}^{-1} \text{dm}^3$ ) <sup>1/2</sup>		
	0.10% (w/v) PVOH	0.35% (w/v) PVOH	0.50% (w/v) PVOH
5% (v/v) methanol			
305	0.2042	1.0888	1.7782
308	0.1626	0.8221	1.4040
313	0.1393	0.7957	1.3735
318	0.1367	0.7741	1.3590
323	0.123	0.7701	1.3381
5% (v/v) ethanol			
305	0.2134	1.0915	1.8107
308	0.2039	1.0082	1.6922
313	0.1555	0.9214	1.6350
318	0.1383	0.8921	1.4679
323	0.1358	0.8295	1.3407
5% (v/v) 2-propanol			
305	0.3468	1.1782	2.1066
308	0.3302	1.1627	1.9176
313	0.3239	1.1516	1.8361
318	0.2814	1.0539	1.7534
323	0.2779	0.9904	1.7184
5% (v/v) 1-butanol			
305	0.4215	1.2276	2.1769
308	0.4140	1.2271	2.0093
313	0.3915	1.1209	1.8998
318	0.3819	1.0559	1.8148
323	0.3426	1.0069	1.7656

TABLE S-V. Continued

Temperature (K)	Ion-Ion interaction (A-coefficient) ( $\text{mol}^{-1} \text{dm}^3$ ) <sup>1/2</sup>		
	0.10% (w/v) PVOH	0.35% (w/v) PVOH	0.50% (w/v) PVOH
Ion-Solvent interaction (B-coefficient) ( $\text{mol}^{-1} \text{dm}^3$ )			
	5% (v/v) methanol		
305	-0.3348	-1.2576	-2.2928
308	-0.2817	-1.0481	-1.8102
313	-0.2386	-1.0109	-1.7189
318	-0.1903	-0.9743	-1.6684
323	-0.1476	-0.8993	-1.6171
	5% (v/v) ethanol		
305	-0.3602	-1.4060	-2.3868
308	-0.3018	-1.3005	-2.1753
313	-0.2513	-1.1766	-2.1552
318	-0.2262	-1.1249	-1.8705
323	-0.1932	-1.0560	-1.7019
	5% (v/v) 2-propanol		
305	-0.5873	-1.5779	-2.8064
308	-0.5189	-1.5358	-2.4956
313	-0.4073	-1.4300	-2.2832
318	-0.4047	-1.3610	-2.2367
323	-0.3941	-1.2463	-2.2352
	5% (v/v) 1-butanol		
305	-0.6444	-1.6705	-2.8148
308	-0.6100	-1.5563	-2.5482
313	-0.5910	-1.4552	-2.5339
318	-0.5320	-1.3829	-2.4042
323	-0.4803	-1.2770	-2.2416

TABLE S-VI. Values of various thermodynamic parameters of 0.1% (w/v) PVOH and 0.5% (w/v) PVOH in different solvents containing acetic acid at 308 K

[CH <sub>3</sub> COOH] (mol dm <sup>-3</sup> )	Ea* (kJ/mol)	ΔG* (kJ/mol)	ΔS* × 10 <sup>-4</sup> (kJ/mol)
0.1% (w/v) PVOH in water			
0.1	16.713	67.908	-0.1662
0.5		67.830	-0.1659
0.5% (w/v) PVOH in water			
0.1	17.864	68.531	-0.1645
0.5		68.201	-0.1634
0.1% (w/v) PVOH in 5% (v/v) methanol			
0.1	16.659	68.065	-0.1669
0.5		67.948	-0.1665

TABLE S-VI. Continued

[CH <sub>3</sub> COOH] (mol dm <sup>-3</sup> )	Ea* (kJ/mol)	ΔG* (kJ/mol)	ΔS* × 10 <sup>-4</sup> (kJ/mol)
0.5% (w/v) PVOH in 5% (v/v) methanol			
0.1	18.146	68.577	-0.1637
0.5		68.253	-0.1627
0.1% (w/v) PVOH in 5% (v/v) ethanol			
0.1	17.223	68.040	-0.1649
0.5		67.934	-0.1646
0.5% (w/v) PVOH in 5% (v/v) ethanol			
0.1	19.223	68.609	-0.1603
0.5		68.234	-0.1591
0.1% (w/v) PVOH in 5% (v/v) 2-propanol			
0.1	17.107	68.153	-0.1647
0.5		68.583	-0.1671
0.5% (w/v) PVOH in 5% (v/v) 2-propanol			
0.1	20.617	68.633	-0.1558
0.5		68.954	-0.1569
0.1% (w/v) PVOH in 5% (v/v) 1-butanol			
0.1	18.854	68.074	-0.1598
0.5		67.892	-0.1592
0.5% (w/v) PVOH in 5% (v/v) butanol			
0.1	20.998	68.645	-0.1547
0.5		68.254	-0.1534