Supporting Information

The Impact of Size and Shape in the Performance of Hydrotropes: A Case-Study of Alkanediols

Dinis O. Abranches,[1†] Bruna P. Soares,[1†] Ana M. Ferreira,[1] Seishi Shimizu,[2] Simão P. Pinho,[3] and João A. P. Coutinho*[1]

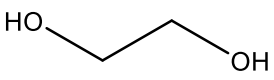
[1]CICECO - Aveiro Institute of Materials, Department of Chemistry, University of Aveiro, Aveiro, Portugal.
[2]York Structural Biology Laboratory, Department of Chemistry, University of York, Heslington, York YO10 5DD, UK.
[3]CIMO, Polytechnic Institute of Bragança, Bragança, Portugal.

*Corresponding Author: João A. P. Coutinho (jcoutinho@ua.pt)

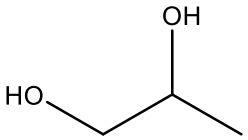
† Equally contributing authors

Contents

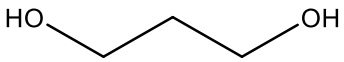
S1. Experimental Solubility Data



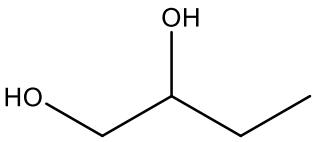
1,2-Ethanediol



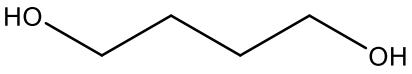
1,2-Propanediol



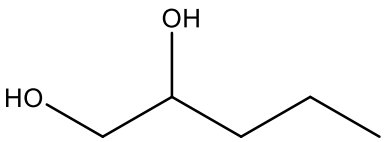
1,3-Propanediol



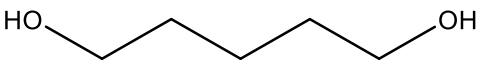
1,2-Butanediol



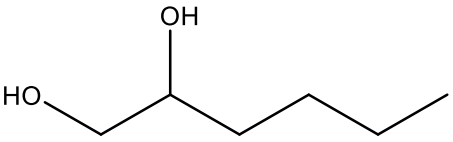
1,4-Butanediol



1,2-Pentanediol

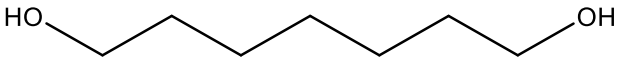


1,5-Pentanediol



1,2-Hexanediol

1,6-Hexanediol



1,7-Heptanediol

Figure S1. *Chemical structure of the alkanediols used in this work as hydrotropes.*

Table S1. *Solubility of syringic acid (S) in aqueous solutions of 1,2-alkanediols (wt % is the weight percentage of alkanediol in water without solute), measured at (303.2 ± 0.5) K, along with the standard uncertainty of each measurement (s, obtained from three independent replicas).*

1,2-Ethanediol			1,2-Propanediol		
wt %	S /g·L^{-1}	s /g·L^{-1}	wt %	S /g·L^{-1}	s /g·L^{-1}
5.08	1.47	0.03	5.00	1.89	0.05
10.01	1.72	0.01	10.03	2.35	0.004
20.37	2.44	0.01	20.03	3.78	0.04
30.13	3.62	0.06	29.97	6.32	0.07
39.97	5.41	0.03	40.00	10.79	0.07
49.84	8.30	0.25	50.02	17.35	0.03
59.65	12.04	0.13	59.85	27.25	0.57
69.70	17.93	0.13	69.83	36.19	0.76
79.62	25.76	0.02	79.91	44.69	0.60
89.55	35.87	0.67	89.96	48.39	0.32
99.90	49.38	0.36	100.00	48.62	0.89
1,2-Butanediol			1,2-Pentanediol		
wt %	S /g·L^{-1}	s /g·L^{-1}	wt %	S /g·L^{-1}	s /g·L^{-1}
5.19	2.02	0.03	5.03	2.75	0.15
10.30	2.95	0.09	10.33	4.88	0.08
20.13	6.71	0.03	20.12	14.78	0.01
30.15	13.69	0.20	29.96	29.61	0.16
40.03	25.20	0.24	40.12	43.69	0.26
49.82	37.69	0.02	50.05	55.80	0.13
59.87	48.89	0.13	59.62	64.73	0.04
69.95	56.70	0.12	69.85	73.68	0.87
79.62	58.61	0.60	79.94	72.11	0.24
89.86	52.27	0.28	89.75	60.77	1.19
100.00	39.22	0.16	100.00	41.08	1.11

1,2-Hexanediol		
wt %	S /g·L^{-1}	s /g·L^{-1}
5.06	3.39	0.04
10.18	7.60	0.24
20.02	15.82	0.06
30.02	23.91	0.06
39.98	32.05	0.29
50.05	40.08	0.12
60.02	47.41	0.19
69.72	52.27	0.31
79.69	53.05	0.21
89.57	46.70	1.81
100.00	35.30	0.69

Table S2. *Solubility of syringic acid (S) in aqueous solutions of 1,n-alkanediols (wt % is the weight percentage of alkanediol in water without solute), measured at (303.2 ± 0.5) K, along with the standard uncertainty of each measurement (s, obtained from three independent replicas).*

1,3-Propanediol			1,4-Butanediol		
wt %	S /g·L^{-1}	s /g·L^{-1}	wt %	S /g·L^{-1}	s /g·L^{-1}
5.12	1.79	0.02	5.14	2.10	0.05
10.06	2.42	0.01	10.21	3.12	0.04
20.32	3.99	0.04	19.92	6.26	0.03
30.06	6.32	0.02	30.12	11.33	0.31
39.76	9.35	0.11	39.87	17.80	0.00
49.88	14.05	0.05	50.07	26.72	0.40
59.76	20.18	0.21	59.73	36.60	0.33
69.49	27.42	0.05	69.59	45.92	0.19
80.05	35.18	0.30	79.10	52.38	0.20
89.82	42.63	0.29	89.37	54.32	0.48
100.00	50.20	0.10	100.00	52.30	0.32
1,5-Pentanediol			1,6-Hexanediol		
wt %	S /g·L^{-1}	s /g·L^{-1}	wt %	S /g·L^{-1}	s /g·L^{-1}
5.03	2.90	0.10	5.03	3.22	0.03
10.16	5.06	0.06	10.15	7.14	0.08
20.21	11.96	0.03	20.02	18.96	0.13
30.11	22.24	0.22	30.05	35.07	0.59
39.99	35.60	0.76	39.82	51.77	0.21
49.97	49.48	0.07	49.84	68.03	0.35
60.04	62.09	0.19	59.99	79.71	0.91
70.01	70.06	0.44	69.55	86.14	1.83
79.89	74.86	0.48	79.87	80.13	0.32
89.95	63.97	1.90	89.34	65.32	0.93
100.00	47.19	0.56			

1,7-Heptanediol		
wt %	S /g·L^{-1}	s /g·L^{-1}
5.05	4.31	0.02
10.10	10.09	0.10
20.03	26.70	0.17
30.08	45.10	0.93
39.99	60.76	0.29
49.78	77.47	0.28
59.87	95.23	1.35
69.11	96.52	0.32
78.02	93.26	1.11
89.46	76.54	2.54
100.00	38.05	1.43

Table S3. *Solubility of pyrene (S) in aqueous solutions of 1,2-pentanediol or 1,5-pentanediol (wt % is the weight percentage of alkanediol in water without solute), measured at (303.2 ± 0.5) K, along with the standard uncertainty of each measurement (s, obtained from three independent replicas).*

1,2-Pentanediol			1,5-Pentanediol		
wt %	S /g·L^{-1}	s /g·L^{-1}	wt %	S /g·L^{-1}	s /g·L^{-1}
20.02	0.021	0.001	20.05	0.0019	0.0001
30.05	0.194	0.003	30.04	0.031	0.004
39.99	0.573	0.017	40.11	0.126	0.009
49.98	1.200	0.010	49.87	0.331	0.004
59.96	2.003	0.011	59.84	0.744	0.019
69.92	3.436	0.003	69.83	1.514	0.021
79.82	5.393	0.054	79.99	2.824	0.154
89.90	8.007	0.190	89.86	5.90	0.093
100.00	13.091	0.394	100.00	10.141	0.760

Table S4. *Solubility of Reichardt's dye (S) in aqueous solutions of 1,2-pentanediol or 1,5-pentanediol (wt % is the weight percentage of alkanediol in water without solute), measured at (303.2 ± 0.5) K, along with the standard uncertainty of each measurement (s, obtained from three independent replicas).*

1,2-Pentanediol			1,5-Pentanediol		
wt %	S /g·L^{-1}	s /g·L^{-1}	wt %	S /g·L^{-1}	s /g·L^{-1}
20.03	0.39	0.02	20.08	0.089	0.002
29.87	1.34	0.06	30.02	0.301	0.005
40.00	3.80	0.07	39.99	0.503	0.03
49.97	9.47	0.20	50.06	1.028	0.05
79.98	21.21	0.83	59.95	2.148	0.036
100.00	45.58	2.96	69.77	5.404	0.264
			79.97	10.468	0.63
			89.96	16.887	0.849
			100.00	41.439	1.58

S2. Setschenow Constants

Table S5. *Setschenow constants for syringic acid and the alkanediols studied in this work obtained from fitting solubility data measured at (303.2 ± 0.5) K (wt % is the weight percentage range of alkanediol in water without solute used in the linear fitting).*

1,2-Alkanediols			1,n-Alkanediols		
Hydrotrope	K_S /kg·mol^{-1}	wt %	Hydrotrope	K_S /kg·mol^{-1}	wt %
1,2-Ethanediol	0.138	0-20	1,3-Propanediol	0.374	0-20
1,2-Propanediol	0.363	0-20	1,4-Butanediol	0.659	0-20
1,2-Butanediol	0.663	0-20	1,5-Pentanediol	1.300	0-10
1,2-Pentanediol	1.206	0-20	1,6-Hexanediol	1.846	0-10
1,2-Hexanediol	1.923	0-10	1,7-Heptanediol	2.589	0-10

S3. Cooperative Model of Hydrotropy

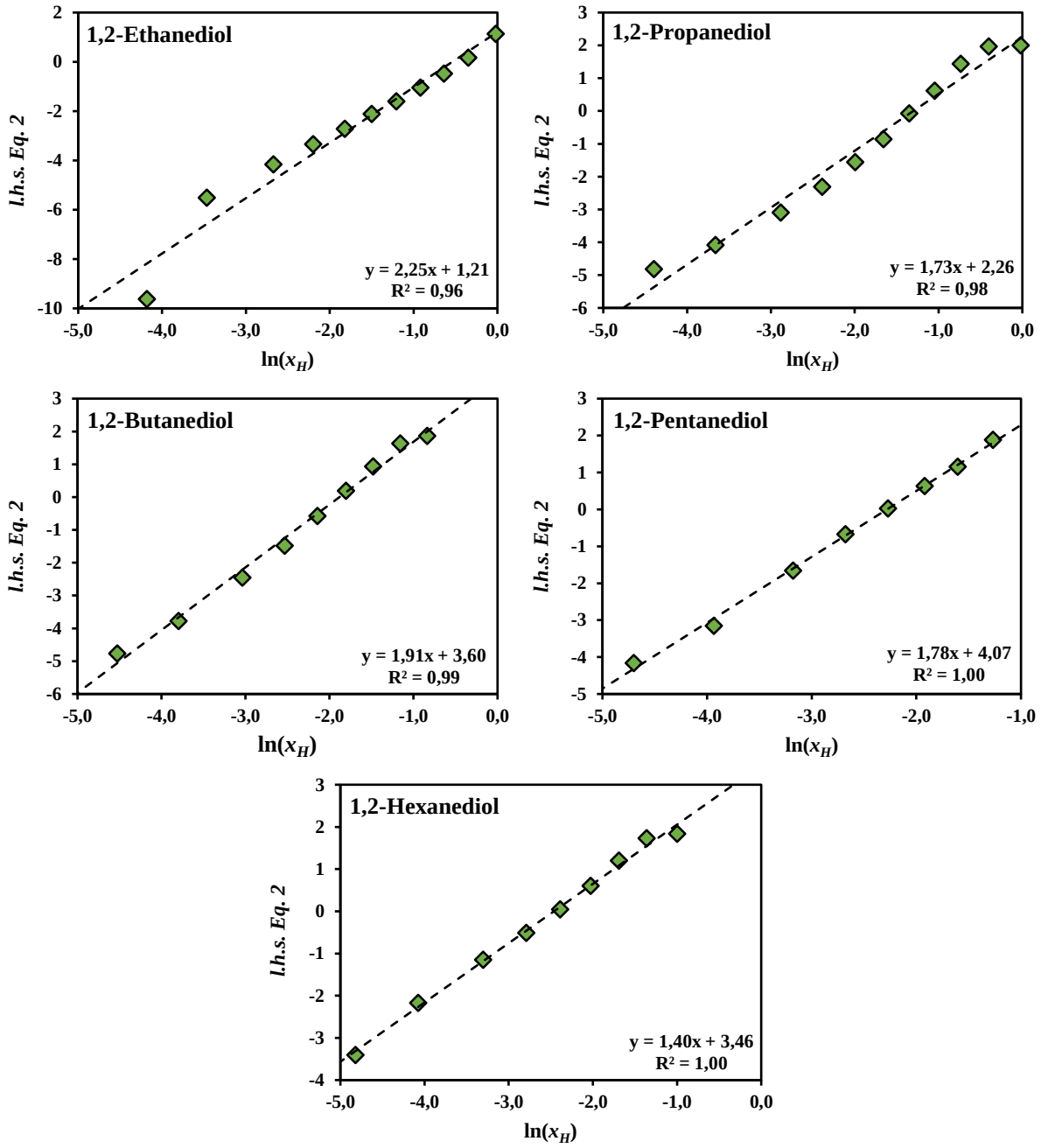


Figure S2. *Left-hand-side of Equation 2 as a function of the natural logarithm of hydrotrope mole fraction in the water/hydrotrope/solute ternary mixture for syringic acid and the 1,2-alkanediols studied in this work at (303.2 ± 0.5) K. Dashed lines represent the best linear fitting obtained using the method of least squares. The slope and intercept of the linear fitting correspond to parameters m and b of the cooperative model of hydrotropy.*

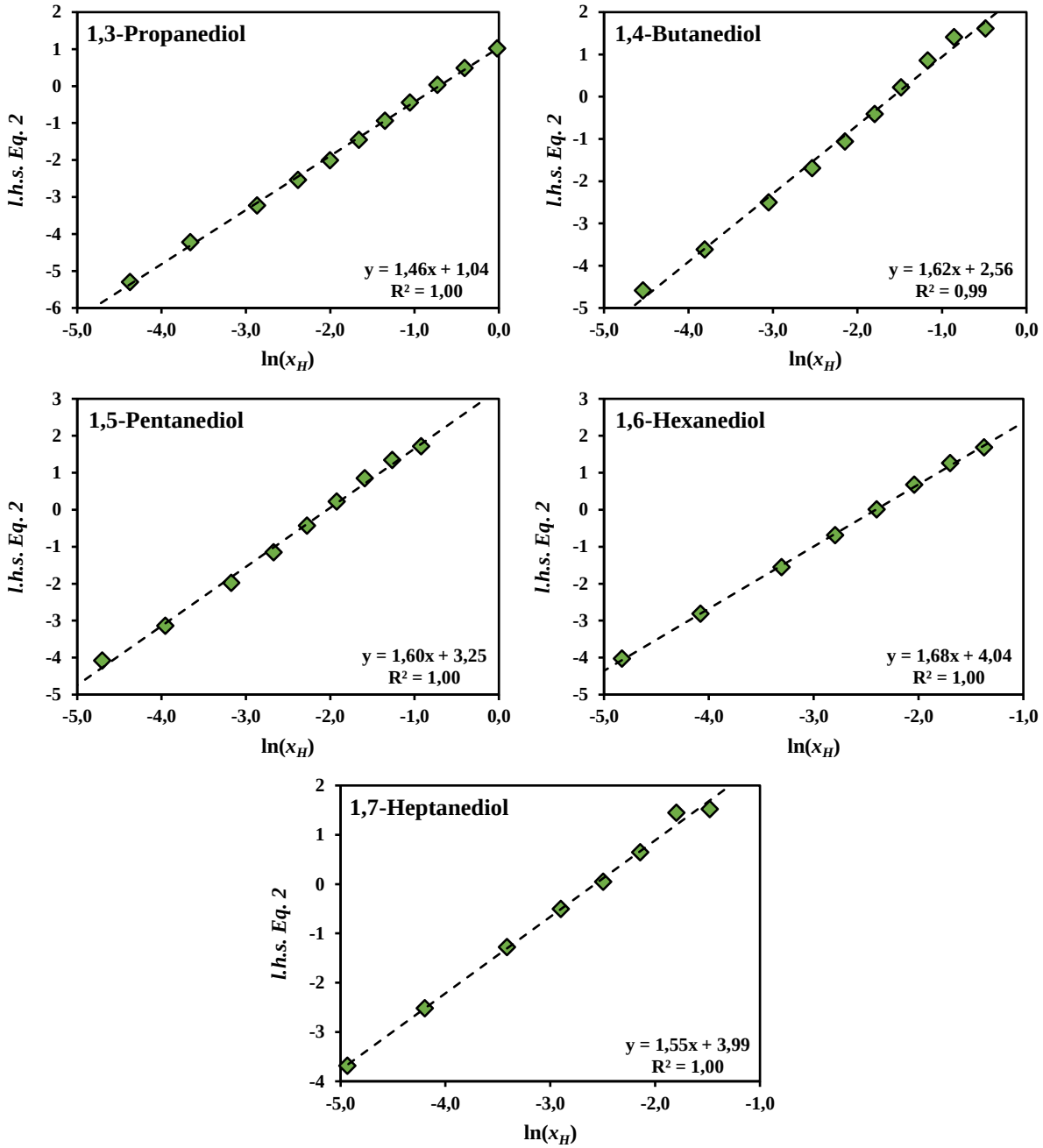


Figure S3. *Left-hand-side of Equation 2 as a function of the natural logarithm of hydrotrope mole fraction in the water/hydrotrope/solute ternary mixture for syringic acid and the 1,n-alkanediols studied in this work at (303.2 ± 0.5) K. Dashed lines represent the best linear fitting obtained using the method of least squares. The slope and intercept of the linear fitting correspond to parameters m and b of the cooperative model of hydrotropy.*

Table S6. *Parameters of the cooperative model of hydrotropy obtained by fitting Equation 2 to the experimental solubility data measured in this work for syringic acid and alkanediols at (303.2 ± 0.5) K.*

1,2-Alkanediols				1,n-Alkanediols			
Hydrotrope	m	b	$(S/S_0)_{max}$	Hydrotrope	m	b	$(S/S_0)_{max}$
1,2-Ethanediol	2.25	1.21	44	1,3-Propanediol	1.46	1.04	46
1,2-Propanediol	1.73	2.26	38	1,4-Butanediol	1.62	2.56	44
1,2-Butanediol	1.91	3.60	46	1,5-Pentanediol	1.60	3.25	60
1,2-Pentanediol	1.78	4.07	58	1,6-Hexanediol	1.68	4.04	70
1,2-Hexanediol	1.40	3.46	42	1,7-Heptanediol	1.55	3.99	80

S4. Polarity Scales

Table S7. *Kamlet-Taft solvatochromic parameter π* for aqueous solutions of 1,2-propanediol and of 1,5-propanediol, experimentally measured in this work at (298.2 ± 0.5) K (wt % is the weight percentage of alkanediol in water).*

1,2-Pentanediol		1,5-Pentanediol	
wt %	π*	wt %	π*
0.00	1.28	0.00	1.28
5.02	1.28	5.08	1.28
10.04	1.28	10.08	1.28
20.03	1.20	20.08	1.28
29.87	1.06	30.02	1.27
40.00	1.04	39.99	1.19
49.97	0.95	50.06	1.14
59.54	0.95	59.95	1.11
70.01	0.89	69.77	1.07
79.98	0.84	79.97	0.98
89.86	0.79	89.96	0.94
100.00	0.65	100.00	0.79

Table S8. *Py scale parameter I_1/I_3 for aqueous solutions of 1,2-propanediol and of 1,5-propanediol, experimentally measured in this work at (298.2 ± 0.5) K (wt % is the weight percentage of alkanediol in water).*

1,2-Pentanediol		1,5-Pentanediol	
wt %	I_1/I_3	wt %	I_1/I_3
0.00	1.892	0.00	1.892
9.95	1.752	19.99	1.581
19.97	1.400	29.96	1.479
30.07	1.316	40.06	1.494
40.07	1.274	49.95	1.462
50.06	1.251	59.96	1.493
59.92	1.265	69.86	1.480
69.93	1.247	79.67	1.494
79.89	1.239	89.75	1.458
89.78	1.233	100.00	1.384
100.00	1.203		