Supplementary Data

(Un)suitability of the use of pH buffers in biological, biochemical and environmental studies and its interaction with metal ions – a review

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Table S1 - Models with the most relevant stability constants (as log β) found in literature for the reviewed buffer/metals. Further information found bellow.

Group		2		6	7		8	9		10		11			12				14	
Type		alkaline earth metal										Transition metal								
Buffer	**Complex**	**Mg(II)**	**Ca(II)**	**Cr(III)**	**Mn(II)**		**Fe(III)**	**Co(II)**		**Ni(II)**		**Cu(II)**			**Zn(II)**		**Cd(II)**		**Pb(II)**	
MES	ML	3.77[1]	4.21[1]		3.48[1]		6.65[2]	3.75[1]	2.04[3]	3.55[1]	2.06[3]	4.90[1]	X[4,5]		3.80[1]	X[5]	X[6]		X[6]	
	$ML(OH)_2$								12.42		12.85									
	ML_2						12.49													
	ML_2OH						23.23													
Bis-Tris	ML	0.34[7a]	2.25[7a]		0.70[7a]			1.78[a], 3.59[7,8]		2.74, 3.59[a 7,8]		5.13[9]			1.94, 2.38[a 7,8]		1.94, 2.47[a 7,8]		4.23[7 a]	
	MLOH											8.01								
	$ML(OH)_2$											20.08								
ADA	ML	3.30[10]	3.29[10]		5.61[10]	4.72[7]		6.34[10]	6.66, 6.72[7,11]	6.80[10]	6.90, 7.68[7,11]	8.28[10]	8.30, 9.7[7,11]		6.45[10]	6.71, 7.10[7,11]	7.08[7b]		8.40[b], 8.73[7,12]	
	ML_2					6.93			9.34, 10.83		11.61, 11.71		12.8, 13.30			9.22, 11.29	10.68		10.64[b], 10.86	
ACES	ML	3.55, 3.72[13,14]	3.38, 4.86[13,14]		3.68-3.85[13–15]			3.49-3.78[13–15]	2.21[7]	3.61-3.85[13–15]	3.12[7]	4.72-5.55[13–15]	4.32[7]	4.38[16]	3.78-4.39[13–15]	2.34[7]				
	ML_2								3.62		5.43		7.77	8.04		3.74				
	ML_2OH													14.93						
	$ML_2(OH)_2$													20.37						
PIPES	ML							3.60[17]	3.12[3]	3.39[17]	3.20[3]	3.75[17]	X[18,19]		3.42[17]	X[20]	X[20,21]		X[20]	
	$ML(OH)_2$								13.30		13.77									
MOPSO	ML						6.92[2]			3.43-3.68[13,14,22]		2.02-4.07[4,13,14,22]	X[5]		X[5]		X[6]		3.50[13]	X[6]
	MLOH						17.81													
	ML_2						13.77													
	ML_2OH						24.63													
BTP	MHL																10.9[23]		11.4[23]	
	ML							4.57[24]		6.97, 7.13[24,25]		10.57[26]	10.7[27]		4.99[24]		4.10		4.7	
	MLOH									12.13, 12.46		18.90	19.4				8.2			
	$ML(OH)_2$									16.36, 16.75		24.27	24.3				10.9			
	ML_2							8.76					18.8		9.18				8.8	
	ML_2OH							13.95					24.7		14.79				14.4	
	$ML_2(OH)_2$							18.83					29.8		19.65				18.4	
BES	ML							3.03[28]				3.51[29]	3.24[27]							
	MLOH												10.9							
	$ML(OH)_2$												16.0							
MOPS	ML	3.51[17]			3.54[22]		7.84[2]	3.39, 3.41[17,22]		3.45[17,22]		4.00, 4.04[17,22]	X[5]		3.47, 3.63[17,22]	X[5]	X[6]		X[6]	
	ML_2						14.82													
	ML_2OH						39.50													
TES	ML			7.35[30]			7.91[2]	2.07[7]		3.35[7b]		3.22[29]	3.90[7]		2.08[7]					
	MLOH									8.55			11.06							
	ML_2			12.78			15.31													
	ML_2OH			19.83			25.72													
	$ML_2(OH)_2$			27.77																
	ML_3			17.18			22.11													
HEPES	MLH											3.22[4,31]	X[4,32]		6.73[33]	X[20]	4.16[33]	X[20]	7.90[33]	X[20]
	ML											7.49			3.27		3.25		3.14	
	MLOH														6.74		6.54		6.79	
	$ML(OH)_2$														13.79		12.27		14.67	
DIPSO	ML	3.42[14]	3.47[14]		3.48-3.76[14,15,22]			3.54-3.63[14,15,22]	2.2[34]	3.61-3.76[14,15,22]	2.7[34]	4.71-4.96[14,15,22]	4.2[35]		3.76-3.83[14,15,22]	2.1[36]	2.9[36]		3.4[37]	
	MLOH								7.6				11.8				6.9			
	$ML(OH)_2$												17.6			13.4				
	ML_2								3.6		4.6		8.1						6.35	
	ML_2OH												14.5						12.8	
	$ML_2(OH)_2$												20.6						18.0	
MOBS	ML						7.77[2]													
	ML_2						15.31													
	ML_2OH						26.05													

Buffer	Complex	Mg(II)	Ca(II)	Cr(III)	Mn(II)	Fe(III)	Co(II)		Ni(II)		Cu(II)			Zn(II)		Cd(II)		Pb(II)
TAPSO	ML	3.37, 3.77[1,14]	3.50, 4.21[1,14]		3.48-3.83[13,14,22]	8.44[2]	3.42-3.53[13,14,22]	2.0[34]	3.48-3.70[13,14,22]	3.0[34]	4.74-5.04[13,14,22]	4.41[38]		3.61-3.80[13,14,22]	2.5[39]	2[39]		3.7[40]
	MLOH							7.8				11.43			7.2			
	$ML(OH)_2$											17.55			13.2			
	ML_2					16.09				4.8		8.08				4.2		6.6
	ML_2OH					26.85						14.3				8.6		12.9
	$ML_2(OH)_2$											20.3						17.8
	ML3					23.22												
Tris	MHL			7.63[30]														
	ML	0.30[7a]	0.25[7 a]			8.59[2]	1.73[7]		2.6[7]		4.05[7]	3.82[41]		2.27[7]		1.88[7]		1.96[7]
	MOH											11.64						
	ML_2			13.63		16.96			4.6		7.6							
	ML_2OH					27.36						15.06						
	$ML_2(OH)_2$											21.47						
	ML_3			18.89		25.12					11.1							
	ML_4										14.1							
HEPPSO	MHL													3.77[33]	X[20]	4.53[33]	X[20]	7.89[33]
	ML	3.69[17]					3.50[17]		3.59[17]		2.05, 5.04[4,17]			3.25		3.28		3.18
	MLOH													6.57		6.69		7.1
	$ML(OH)_2$													12.93		9.4		14.24
TEA	ML	0.24[7a]	0.78[7 a]				2.55[7]		2.76[7]		4.07[7]			2.05[7]		2.70[7]		3.39[7]
	MLOH										12.44							
	$ML(OH)_2$																	16.44
	ML_2								3.6					3.28		4.60		5.86
	ML_2OH										14.43							
	$M_2L_2(OH)_2$								18.28[c]		28.08[c]							20.61
	ML_3															5.21		
EPPS	ML										2.90[42]			X[42]		X[42]		3.1[42]
Tricine	ML	4.22[10]	4.69[10]				4.63, 5.44[10,43]	4.58[11]	5.21, 5.48[10,43]	6.27[11]	7.58, 7.64[10,43]	7.40[11]		6.23[10]	5.11[11]			
	ML_2							8.06		10.07		11.51			8.78			
Bicine	ML	4.05[10]	4.13[10]		3.07[7]	4.27[2]	4.92, 5.91[10,44]	5.30, 5.52[7,11]	4.69, 6.85[10,44]	6.42, 6.56[7,11]	7.23-8.31[10,11,29,44]	8.24[11]	8.07[7]	5.29[10]	5.37, 5.71[7,11]	4.28[7]		
	MLOH												15.05					
	$ML(OH)_2$					30.01												
	$MLOH_3$					38.0												
	ML_2				5.32	7.35		8.86, 8.96		10.67, 10.74		13.06	13.47		8.57, 9.25	8.28		
TAPS	ML			7.51[30]		8.53[2]					5.62[29]	4.2[45]		2.4[36]		2.50[36]		3.27[46]
	$ML(OH)_2$													12.9				
	ML_2			12.78		16.78						7.8						6.5
	ML_2OH					27.24						13.9						12.7
	$ML_2(OH)2$											18.94						17.27
	ML_3					24.86												
AMPD	ML										4.44[41]							
	MLOH										11.49							
	ML_2OH										15.36							
	$ML_2(OH)_2$										21.02							
TABS	ML					9.75[2]												
	ML2					18.84												
	ML2OH					29.14												
	ML3					27.74												
AMPSO	ML						3.42, 3.52[15,17]		3.58, 3.62[15,17]		5.30[15,17]	4.62[47]		4.30, 4.42[15,17]	2.5[48]	2.1[48]		2.9[37]
	MLOH											11.7				6.2		9.4
	$ML(OH)_2$														12.9			14.5
	ML_2											9.5						
	ML_2OH											15.6						
	$ML_2(OH)_2$											21.2						
	ML_3											13.4						
CHES	ML	3.84-4.28[1,14]	3.86-4.64[1,14]		4.93[1]		4.58[1]											4.78[1]

The previous table contains the models with the most relevant stability constants (as log β, according to the formula present in the introduction section from the paper) found in literature for the reviewed buffer/metals. If two values are found for the same species inside the same model, these are placed in ascending order, if more than two are found, a range is displayed. Models are ordered in chronological/complexity from left to right. The reference at the top of the model is valid for all species bellow in that model. Unless stated otherwise (see notes below), stability constant values are valid for 25ºC and μ = 0.1 M. Buffers POPSO, HEPBS, CAPSO, AMP, CAPS and CABS were omitted due to the lack of published data.

Notes: a - μ = 1.0 M; b - t = 20ºC; c - μ = 0.5M

Bibliography:

1. H. A. Azab and Z. M. Anwar, *J. Chem. Eng. Data*, 2012, **57**, 2890–2895.

2. B. S. Gupta, M. Taha and M. Lee, *J. Solution Chem.*, 2013, **42**, 2296–2309.

3. D. Wyrzykowski, B. Pilarski, D. Jacewicz and L. Chmurzyński, *J. Therm. Anal. Calorim.*, 2012, **111**, 1829–1836.

4. H. E. Mash, Y. Chin, L. Sigg, R. Hari and H. Xue, *Anal. Chem.*, 2003, **75**, 671–677.

5. H. M. V. M. Soares, S. C. Pinho and M. G. R. T. M. Barros, *Electroanalysis*, 1999, **11**, 1312–1317.

6. H. M. V. M. Soares, P. C. F. L. Conde, A. A. N. Almeida and M. T. S. D. Vasconcelos, *Anal. Chim. Acta*, 1999, **394**, 325–335.

7. A. E. Martell and R. M. Smith, NIST Standard Reference Database 46 Version 8.0, NIST Critically Selected Stability Constants of Metal Complexes Database, U.S. Department of Commerce; National Institute of Standards and Technology: Gaithersburg, MD, 2004.

8. K. H. Scheller, T. H. J. Abel, P. E. Polanyi, P. K. Wenk, B. E. Fischer and H. Sigel, *Eur. J. Biochem.*, 1980, **107**, 455–466.

9. K. H. Hong, E. J. Ha and K. S. Bai, *Bull. Korean Chem. Soc.*, 1995, **16**, 406–409.

10. H. A. Azab, Z. M. Anwar and M. Sokar, *J. Chem. Eng. Data*, 2004, **49**, 62–72.

11. M. M. Khalil, A. M. Radalla and A. G. Mohamed, *J. Chem. Eng. Data*, 2009, **54**, 3261–3272.

12. H. A. Azab, *Monatshefte für Chemie Chem. Mon.*, 1992, **123**, 1107–1115.

13. Z. M. Anwar and H. A. Azab, *J. Chem. Eng. Data*, 2001, **46**, 34–40.

14. H. A. Azab, F. S. Deghaidy, A. S. Orabi and N. Y. Farid, *J. Chem. Eng. Data*, 2000, **45**, 709–715.

15. M. Taha, R. A. Saqr and A. T. Ahmed, *J. Chem. Thermodyn.*, 2007, **39**, 304–308.

16. I. Zawisza, M. Rózga, J. Poznański and W. Bal, *J. Inorg. Biochem.*, 2013, **129**, 58–61.

17. H. A. Azab, A. S. Orabi and E.-S. E. T. Abd, *J. Chem. Eng. Data*, 2001, **46**, 346–354.

18. M. T. S. D. Vasconcelos, M. A. Azenha and C. M. R. Almeida, *Anal. Biochem.*, 1998, **265**, 193–201.

19. M. T. S. D. Vasconcelos and C. M. R. Almeida, *Anal. Chim. Acta*, 1998, **369**, 115–122.

20. H. M. V. M. Soares and P. C. F. L. Conde, *Anal. Chim. Acta*, 2000, **421**, 103–111.

21. D. R. Hoffman, J. L. Okon and T. R. Sandrin, *Chemosphere*, 2005, **59**, 919–927.

22. Z. M. Anwar and H. A. Azab, *J. Chem. Eng. Data*, 1999, **44**, 1151–1157.

23. C. M. H. Ferreira, I. S. S. Pinto, A. Amoresano, S. M. Sadeghi and H. M. V. M. Soares, *J. Coord. Chem.*, 2014, **67**, 3354–3370.

24. T. Laureys, I. S. S. Pinto, C. V. M. Soares, H. B. Boppudi and H. M. V. M. Soares, *J. Chem. Eng. Data*, 2012, **57**, 87–92.

25. K. S. Bai and K. H. Hong, *Bull. Korean Chem. Soc.*, 2000, **21**, 650–652.

26. K. H. Hong and K. S. Bai, *Bull. Korean Chem. Soc.*, 1998, **19**, 197–201.

27. S. M. Sadeghi, C. M. H. Ferreira, S. Vandenbogaerde and H. M. V. M. Soares, *J. Coord. Chem.*, 2015, **68**, 777–793.

28. H. A. Azab, A. M. El-Nady, S. A. El-Korashy and M. M. A. Hamed, *J. Chem. Eng. Data*, 1995, **40**, 83–87.

29. H. A. Azab and A. M. El-Nady, *Monatshefte für Chemie Chem. Mon.*, 1994, **125**, 849–858.

30. M. Taha, B. S. Gupta and M. Lee, *J. Chem. Eng. Data*, 2011, **56**, 3541–3551.

31. M. Sokołowska and W. Bal, *J. Inorg. Biochem.*, 2005, **99**, 1653–1660.

32. M. Renganathan and S. Bose, *Photosynth. Res.*, 1990, **23**, 95–99.

33. Z. M. Anwar, *J. Chinese Chem. Soc.*, 2005, **52**, 863–871.

34. C. M. M. Machado, P. Gameiro and H. M. V. M. Soares, *J. Solution Chem.*, 2008, **37**, 603–617.

35. C. M. M. Machado, S. Scheerlinck, I. Cukrowski and H. M. V. M. Soares, *Anal. Chim. Acta*, 2004, **518**, 117–126.

36. C. M. M. Machado, G. M. S. Alves, I. S. S. Pinto, S. Scheerlinck, S. Van Acker and H. M. V. M. Soares, *J. Solution Chem.*, 2013, **42**, 1602–1619.

37. M. Eliat-Eliat, I. S. S. Pinto, G. M. S. Alves, V. Olle and H. M. V. M. Soares, *J. Coord. Chem.*, 2013, **66**, 3544–3560.

38. C. M. M. Machado and H. M. V. M. Soares, *Talanta*, 2003, **71**, 1352–1363.

39. C. M. M. Machado, I. Cukrowski and H. M. V. M. Soares, *Talanta*, 2006, **68**, 819–830.

40. C. M. M. Machado, I. Cukrowski and H. M. V. M. Soares, *Electroanalysis*, 2005, **17**, 1291–1301.

41. S. Canepari, V. Carunchio and R. Schina, *Polyhedron*, 1999, 18, 3263–3267.

42. H. M. V. M. Soares and M. G. R. T. M. Barros, *Electroanalysis*, 2001, **13**, 325–331.

43. M. M. Khalil and M. Taha, *Monatshefte für Chemie Chem. Mon.*, 2004, **135**, 385–395.

44. M. Taha, M. M. Khalil and S. A. Mohamed, *J. Chem. Eng. Data*, 2005, **50**, 882–887.

45. C. M. M. Machado and H. M. V. M. Soares, *Talanta*, 2007, **71**, 1352–1363.

46. C. M. M. Machado, O. Victoor and H. M. V. M. Soares, *Talanta*, 2007, **71**, 1326–1332.

47. C. M. M. Machado, I. Cukrowski and H. M. V. M. Soares, *Helv. Chim. Acta*, 2003, **86**, 3288–3304.

48. C. M. M. Machado, I. Cukrowski and H. M. V. M. Soares, *Electroanalysis*, 2006, **18**, 719–729.