Supporting Information

Simultaneous Determination of All Species Concentrations in Multi-Equilibria for Aqueous Solutions of Dihydrogen Phosphate Considering Debye-Hückel Theory

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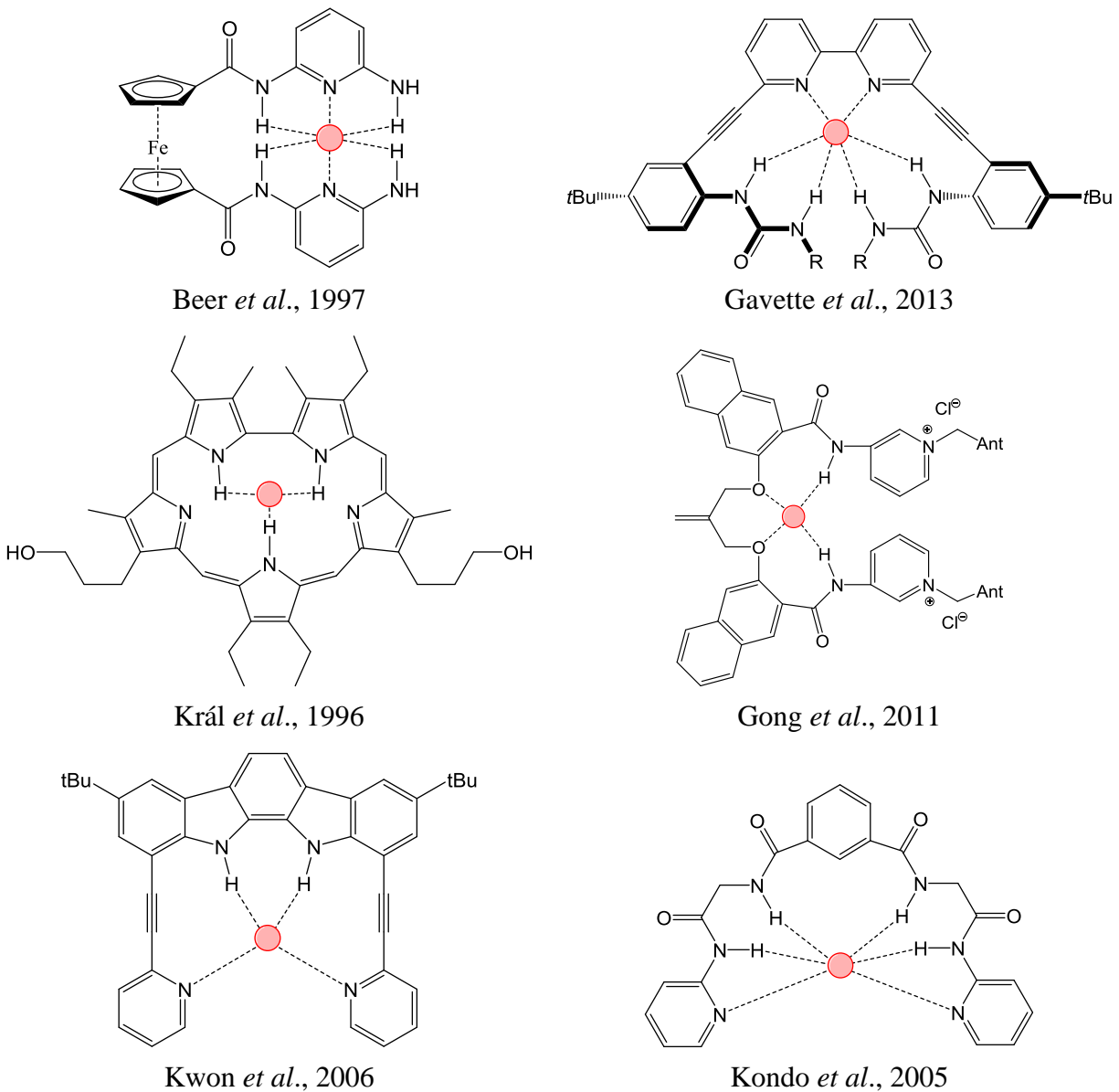
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Figure S1. Examples of selective optical sensors for detection $H_2PO_4^-$. Red circles indicate the binding site of $H_2PO_4^-$.

Comparison to Equilibrium Method

We compared the results obtained with the dynamical approach to the result computed with the equilibrium approach via the iterative solution of the equilibrium equations with the add-in *Solver* tool in Microsoft Excel.[4,5] To fully describe the equilibria one needs at least as many equations as there are *species* in the solution. The number of species exceeds the number of equilibrium equations and balance equations are needed to make up for the difference. There is one mass balance equation for acid H_3A and its conjugate bases and a second mass balance equation for acid H_3B and its conjugate bases. Also, there is one charge balance equation.

Four convenient "variables" were chosen and they are: IS, $[H^+]$, $[H_3A]$, and $[HB^{2-}]$. The initial conditions, pK_a values, and the Davies equations (with $b = 0.1$) for the activity coefficients were all specified and all other species concentrations were thus defined algebraically in terms of the four variables. An error function is expressed as the difference between the mathematical definition of the parameter and the current value that parameter. The magnitude of the value in the "balance equation cell" is a measure of how far the system is from equilibrium. The composite error function employed here is defined as the sum of the errors of the balance equations and of the ionic strength error function. Each individual error function is squared to maintain a positive value. The composite error function is advantageous because it includes many of the ionic species and this sensitivity allows for faster and smoother convergence to the equilibrium. The composite error cell is used as the objective cell in the *Solver* tool and is minimized via manipulation of the variable cells.

After running the *Solver* tool, some of the data generated were not physically realistic (e.g., the sum of output concentrations of all A-containing species exceeded $[H_3A]_0$). Therefore, the following constraints were added to the *Solver* tool: (1) $H_{inp} = H_{out}$, (2) $A_{inp} = A_{out}$, (3) $B_{inp} = B_{out}$, (4) IS > 0, where A_{inp} is equal to $[H_3A]_0$, B_{inp} is $[HB^{2-}]_0$, and H_{inp} is $3 \times [H_3A]_0 + [HB^{2-}]_0 + [H^+]_0$ and A_{out} is $[H_3A] + [H_2A^-] + [HA^{2-}] + [A^{3-}]$ and similarly for B_{out} and H_{out}. With these additional inputs, the calculated pH_{act} is in good agreement with the results of the dynamical

approach and with experiment. Tables 1 and S1 and S4 include pH values obtained with this method.

The method is helpful because it numerically approximates the pH, but it is pragmatically unsophisticated; non-variable species concentrations and balance equations are defined and computed algebraically, and the user must perform all of the algebra and cell-selecting. This is not trivial because it means that expanding the method or describing a new system/adding a new species involves reconstruction of a major portion of the spreadsheet. Also, results are obtained one at a time with no scalability for large data sets, making recalculation for new or adjusted systems rather tedious.
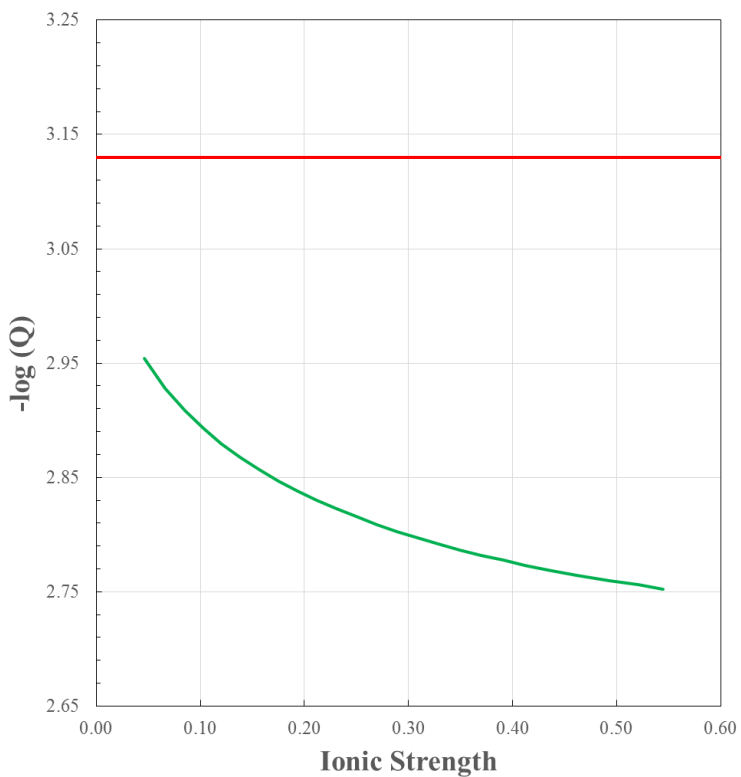
Figure S2. Negative logarithm of the concentration quotient, pQ_1 (green) for the first dissociation of citric acid shown as a function of ionic strength and compared to the pK_a at infinite dilution, pK_1 (red), using the data for the citric acid/hydrogenphosphate mixtures. The pQ_1 curve begins at IS = 0.05 M which corresponds to the most acidic mixture studied.

Table S1. Reported and Calculated pH values and Ionic Strength for a Series of Mixtures[a] of the Buffer Solution

	$[H_3Cit]_0$	$[HPO_4^{2-}]_0$	Expt.[8]	$f = 1$		$b = 0.1$		$b = 0.2$		Lit.[b]	Ionic Strength		
Mix.	[mol/L]	[mol/L]	pH	pH_{conc}	pH_{act}	pH_{conc}	pH_{act}	pH_{conc}	pH_{act}	pH_{act}	$f = 1$	$b = 0.1$	$b = 0.2$
1	0.098	0.004	2.2	2.25	2.30	2.18	2.23	2.18	2.23	2.23	0.01	0.01	0.01
2	0.094	0.012	2.4	2.53	2.60	2.41	2.48	2.41	2.48	2.48	0.03	0.03	0.03
3	0.089	0.022	2.6	2.77	2.86	2.61	2.70	2.61	2.70	2.70	0.05	0.05	0.05
4	0.084	0.032	2.8	3.00	3.10	2.80	2.90	2.80	2.90	2.90	0.07	0.07	0.07
5	0.079	0.041	3.0	3.21	3.32	2.98	3.09	2.99	3.09	3.09	0.08	0.09	0.09
6	0.075	0.049	3.2	3.41	3.53	3.15	3.26	3.16	3.27	3.26	0.10	0.10	0.10
7	0.072	0.057	3.4	3.63	3.75	3.32	3.45	3.34	3.45	3.45	0.12	0.12	0.12
8	0.068	0.064	3.6	3.89	4.01	3.51	3.64	3.53	3.66	3.64	0.14	0.14	0.14
9	0.065	0.071	3.8	4.15	4.28	3.70	3.84	3.73	3.86	3.84	0.15	0.16	0.16
10	0.061	0.077	4.0	4.40	4.53	3.89	4.03	3.92	4.05	4.03	0.17	0.17	0.17
11	0.059	0.083	4.2	4.63	4.77	4.07	4.22	4.11	4.25	4.22	0.19	0.19	0.19
12	0.056	0.088	4.4	4.87	5.01	4.26	4.41	4.31	4.44	4.41	0.21	0.21	0.21
13	0.053	0.094	4.6	5.13	5.27	4.47	4.62	4.52	4.66	4.62	0.23	0.23	0.23
14	0.051	0.099	4.8	5.42	5.57	4.69	4.85	4.75	4.89	4.85	0.25	0.25	0.25
15	0.049	0.103	5.0	5.70	5.84	4.90	5.06	4.96	5.11	5.06	0.27	0.27	0.27
16	0.046	0.107	5.2	5.93	6.08	5.09	5.26	5.17	5.32	5.26	0.29	0.29	0.29
17	0.044	0.112	5.4	6.14	6.29	5.29	5.46	5.37	5.52	5.46	0.31	0.31	0.31
18	0.042	0.116	5.6	6.33	6.48	5.49	5.66	5.57	5.73	5.66	0.33	0.33	0.33
19	0.040	0.121	5.8	6.51	6.66	5.69	5.86	5.78	5.93	5.86	0.35	0.35	0.35
20	0.037	0.126	6.0	6.68	6.83	5.89	6.06	5.98	6.13	6.06	0.37	0.37	0.37
21	0.034	0.132	6.2	6.84	7.00	6.08	6.25	6.16	6.32	6.25	0.39	0.39	0.39
22	0.031	0.139	6.4	7.00	7.15	6.24	6.42	6.33	6.49	6.42	0.41	0.41	0.41
23	0.027	0.146	6.6	7.15	7.31	6.41	6.59	6.50	6.65	6.59	0.43	0.43	0.43
24	0.023	0.155	6.8	7.34	7.50	6.59	6.78	6.69	6.85	6.78	0.46	0.46	0.46
25	0.018	0.165	7.0	7.55	7.71	6.80	6.98	6.90	7.06	6.98	0.49	0.49	0.49
26	0.013	0.174	7.2	7.75	7.92	7.00	7.19	7.11	7.27	7.19	0.52	0.52	0.52
27	0.009	0.182	7.4	7.96	8.13	7.21	7.39	7.32	7.48	7.39	0.54	0.55	0.54
28	0.006	0.187	7.6	8.16	8.32	7.40	7.59	7.51	7.67	7.59	0.56	0.56	0.56
29	0.004	0.192	7.8	8.36	8.52	7.59	7.78	7.71	7.87	7.78	0.57	0.57	0.57
30	0.003	0.195	8.0	8.56	8.72	7.80	7.99	7.91	8.08	7.99	0.58	0.58	0.58

a) Volumes of buffer solutions given in ref. 8 were converted to concentrations and used as initial values in the various approaches.
b) Calculated using the method described in ref. 5 with modifications.

Table S2a. Calculated Citrate Species Concentrations[a] at Equilibrium for the Series of Mixtures of Buffer Solution

Mix.	[H_3Cit] $f = 1$	[H_3Cit] $b = 0.1$	[H_3Cit] $b = 0.2$	[H_2Cit^-] $f = 1$	[H_2Cit^-] $b = 0.1$	[H_2Cit^-] $b = 0.2$	[$HCit^{2-}$] $f = 1$	[$HCit^{2-}$] $b = 0.1$	[$HCit^{2-}$] $b = 0.2$	[Cit^{3-}] $f = 1$	[Cit^{3-}] $b = 0.1$	[Cit^{3-}] $b = 0.2$
1	86.6	85.7	85.7	11.4	12.3	12.2	0.0	0.1	0.1	0.0	0.0	0.0
2	74.9	74.1	74.1	18.8	19.6	19.5	0.1	0.2	0.2	0.0	0.0	0.0
3	61.6	61.1	61.1	27.2	27.6	27.6	0.3	0.4	0.4	0.0	0.0	0.0
4	48.0	47.8	47.8	35.5	35.4	35.4	0.6	1.0	1.0	0.0	0.0	0.0
5	35.6	35.8	35.8	42.7	41.8	41.8	1.2	1.9	1.9	0.0	0.0	0.0
6	25.1	25.8	25.7	48.1	46.2	46.3	2.2	3.3	3.3	0.0	0.0	0.0
7	16.2	17.5	17.5	51.4	48.4	48.5	3.8	5.6	5.5	0.0	0.0	0.0
8	9.1	10.8	10.7	51.8	47.8	48.1	6.9	9.1	8.9	0.0	0.1	0.1
9	4.6	6.3	6.2	48.1	44.3	44.6	11.7	13.7	13.5	0.1	0.2	0.2
10	2.2	3.5	3.4	41.2	38.5	38.7	17.9	19.1	19.0	0.2	0.4	0.4
11	1.0	1.8	1.8	32.7	31.3	31.4	24.5	24.6	24.6	0.4	0.9	0.8
12	0.4	0.9	0.8	23.9	23.6	23.6	30.7	29.7	29.8	0.9	1.7	1.6
13	0.2	0.4	0.3	15.3	16.0	15.9	35.9	33.6	33.8	1.9	3.3	3.2
14	0.0	0.1	0.1	8.3	9.6	9.5	38.3	34.9	35.2	4.1	6.0	5.8
15	0.0	0.0	0.0	4.3	5.6	5.4	36.9	33.3	33.6	7.3	9.6	9.4
16	0.0	0.0	0.0	2.2	3.0	2.9	32.9	29.4	29.7	11.2	13.9	13.7
17	0.0	0.0	0.0	1.1	1.5	1.5	27.7	24.0	24.4	15.4	18.7	18.4
18	0.0	0.0	0.0	0.6	0.7	0.7	22.3	18.2	18.6	19.1	23.1	22.7
19	0.0	0.0	0.0	0.3	0.3	0.3	17.2	12.7	13.1	22.1	26.6	26.1
20	0.0	0.0	0.0	0.2	0.1	0.1	12.7	8.3	8.7	24.0	28.4	28.0
21	0.0	0.0	0.0	0.1	0.1	0.1	9.0	5.3	5.6	24.8	28.6	28.2
22	0.0	0.0	0.0	0.0	0.0	0.0	6.2	3.3	3.6	24.5	27.4	27.1
23	0.0	0.0	0.0	0.0	0.0	0.0	4.1	2.1	2.2	23.1	25.2	25.0
24	0.0	0.0	0.0	0.0	0.0	0.0	2.3	1.1	1.2	20.4	21.6	21.5
25	0.0	0.0	0.0	0.0	0.0	0.0	1.2	0.5	0.6	16.5	17.1	17.1
26	0.0	0.0	0.0	0.0	0.0	0.0	0.6	0.2	0.3	12.5	12.8	12.8
27	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.1	0.1	8.9	9.0	9.0
28	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.1	6.2	6.3	6.3
29	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	4.2	4.2	4.2
30	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	2.7	2.7	2.7

a) Concentrations in mmol/L. Data computed for the mixtures listed in Table S1.

Table S2b. Calculated Phosphate Species Concentrations[a] at Equilibrium for the Series of Mixtures of Buffer Solution

Mix.	[H_3PO_4] $f = 1$	$b = 0.1$	$b = 0.2$	[$H_2PO_4^-$] $f = 1$	$b = 0.1$	$b = 0.2$	[HPO_4^{2-}] $f = 1$	$b = 0.1$	$b = 0.2$	[PO_4^{3-}] $f = 1$	$b = 0.1$	$b = 0.2$
1	1.8	1.7	1.7	2.2	2.3	2.3	0.0	0.0	0.0	0.0	0.0	0.0
2	3.7	3.6	3.6	8.7	8.8	8.8	0.0	0.0	0.0	0.0	0.0	0.0
3	4.3	4.2	4.2	17.5	17.6	17.6	0.0	0.0	0.0	0.0	0.0	0.0
4	4.0	4.0	4.0	27.7	27.7	27.7	0.0	0.0	0.0	0.0	0.0	0.0
5	3.4	3.5	3.4	37.7	37.6	37.6	0.0	0.0	0.0	0.0	0.0	0.0
6	2.6	2.8	2.8	46.8	46.6	46.6	0.0	0.0	0.0	0.0	0.0	0.0
7	1.9	2.1	2.1	55.1	54.8	54.9	0.0	0.0	0.0	0.0	0.0	0.0
8	1.2	1.5	1.5	63.2	62.8	62.9	0.0	0.0	0.0	0.0	0.0	0.0
9	0.7	1.1	1.0	70.2	69.9	69.9	0.1	0.1	0.1	0.0	0.0	0.0
10	0.4	0.7	0.7	76.5	76.2	76.2	0.1	0.1	0.1	0.0	0.0	0.0
11	0.3	0.5	0.5	82.3	82.1	82.1	0.2	0.2	0.2	0.0	0.0	0.0
12	0.2	0.3	0.3	87.6	87.5	87.5	0.4	0.4	0.4	0.0	0.0	0.0
13	0.1	0.2	0.2	92.6	92.6	92.6	0.8	0.7	0.7	0.0	0.0	0.0
14	0.1	0.1	0.1	97.0	97.2	97.2	1.6	1.3	1.3	0.0	0.0	0.0
15	0.0	0.1	0.1	99.9	100.8	100.7	3.1	2.1	2.2	0.0	0.0	0.0
16	0.0	0.1	0.1	101.8	103.6	103.4	5.4	3.6	3.7	0.0	0.0	0.0
17	0.0	0.0	0.0	102.7	105.6	105.3	8.8	5.9	6.1	0.0	0.0	0.0
18	0.0	0.0	0.0	102.4	106.4	106.0	13.5	9.6	10.0	0.0	0.0	0.0
19	0.0	0.0	0.0	100.8	105.3	104.9	20.1	15.5	16.0	0.0	0.0	0.0
20	0.0	0.0	0.0	97.6	102.0	101.6	28.7	24.3	24.7	0.0	0.0	0.0
21	0.0	0.0	0.0	92.6	96.3	96.0	39.6	35.9	36.2	0.0	0.0	0.0
22	0.0	0.0	0.0	86.0	88.9	88.6	52.5	49.6	49.9	0.0	0.0	0.0
23	0.0	0.0	0.0	77.6	79.7	79.5	67.9	65.8	66.0	0.0	0.0	0.0
24	0.0	0.0	0.0	65.9	67.1	67.0	88.6	87.4	87.5	0.0	0.0	0.0
25	0.0	0.0	0.0	51.8	52.4	52.4	112.9	112.3	112.3	0.0	0.0	0.0
26	0.0	0.0	0.0	38.6	38.9	38.9	135.3	135.0	135.0	0.0	0.0	0.0
27	0.0	0.0	0.0	27.2	27.4	27.3	154.5	154.3	154.3	0.0	0.0	0.0
28	0.0	0.0	0.0	19.0	19.0	19.0	168.3	168.2	168.3	0.0	0.0	0.0
29	0.0	0.0	0.0	12.7	12.8	12.8	178.8	178.7	178.7	0.0	0.0	0.0
30	0.0	0.0	0.0	8.3	8.3	8.3	186.2	186.1	186.1	0.0	0.1	0.1

a) Concentrations in mmol/L. Data computed for the mixtures listed in Table S1.

Table S3. Reported and Calculated pH values and Ionic Strength for a Series of Mixtures[a] of the Buffer Solution

Mix.	$[H_3Cit]_0$ [mol/L]	$[HPO_4^{2-}]_0$ [mol/L]	Expt.[9] pH	$f = 1$ pH_{conc}	pH_{act}	Davies pH_{conc}	pH_{act}	Lit.[b] pH_{act}	Ionic Strength $f = 1$	Davies
1	0.089	0.022	2.6	2.77	2.86	2.61	2.70	2.70	0.05	0.05
2	0.084	0.032	2.8	3.00	3.10	2.80	2.90	2.90	0.07	0.07
3	0.079	0.041	3.0	3.21	3.32	2.98	3.09	3.09	0.08	0.09
4	0.075	0.049	3.2	3.41	3.53	3.15	3.26	3.26	0.10	0.10
5	0.072	0.057	3.4	3.63	3.75	3.32	3.45	3.45	0.12	0.12
6	0.068	0.064	3.6	3.89	4.01	3.51	3.64	3.64	0.14	0.14
7	0.065	0.071	3.8	4.15	4.28	3.70	3.84	3.84	0.15	0.16
8	0.061	0.077	4.0	4.40	4.53	3.89	4.03	4.03	0.17	0.17
9	0.059	0.083	4.2	4.63	4.77	4.07	4.22	4.22	0.19	0.19
10	0.056	0.088	4.4	4.87	5.01	4.26	4.41	4.41	0.21	0.21
11	0.053	0.094	4.6	5.13	5.27	4.47	4.62	4.62	0.23	0.23
12	0.051	0.099	4.8	5.42	5.57	4.69	4.85	4.85	0.25	0.25
13	0.049	0.103	5.0	5.70	5.84	4.90	5.06	5.06	0.27	0.27
14	0.046	0.107	5.2	5.93	6.08	5.09	5.26	5.26	0.29	0.29
15	0.044	0.112	5.4	6.14	6.29	5.29	5.46	5.46	0.31	0.31
16	0.042	0.116	5.6	6.33	6.48	5.49	5.66	5.66	0.33	0.33
17	0.040	0.121	5.8	6.51	6.66	5.69	5.86	5.86	0.35	0.35
18	0.037	0.126	6.0	6.68	6.83	5.89	6.06	6.06	0.37	0.37
19	0.034	0.132	6.2	6.84	7.00	6.08	6.25	6.25	0.39	0.39
20	0.031	0.139	6.4	7.00	7.15	6.24	6.42	6.42	0.41	0.41
21	0.027	0.146	6.6	7.15	7.31	6.41	6.59	6.59	0.43	0.43
22	0.023	0.155	6.8	7.34	7.50	6.59	6.78	6.78	0.46	0.46
23	0.018	0.165	7.0	7.55	7.71	6.80	6.98	6.98	0.49	0.49
24	0.013	0.174	7.2	7.75	7.92	7.00	7.19	7.19	0.52	0.52
25	0.009	0.182	7.4	7.96	8.13	7.21	7.39	7.39	0.54	0.55

a) Volumes of buffer solutions given in ref. 9 were converted to concentrations and used as initial values in the various approaches.
b) Calculated using the method described in ref. 5 with modifications.

Table S4a. Calculated Citrate Species Concentrations[a] at Equilibrium for the Series of Mixtures of Buffer Solution

Mix.	[H₃Cit]			[H₂Cit⁻]			[HCit²⁻]			[Cit³⁻]		
	$f = 1$	$b = 0.1$	$b = 0.2$	$f = 1$	$b = 0.1$	$b = 0.2$	$f = 1$	$b = 0.1$	$b = 0.2$	$f = 1$	$b = 0.1$	$b = 0.2$
1	61.6	61.1	61.1	27.2	27.6	27.6	0.3	0.4	0.4	0.0	0.0	0.0
2	48.0	47.8	47.8	35.5	35.4	35.4	0.6	1.0	1.0	0.0	0.0	0.0
3	35.6	35.8	35.8	42.7	41.8	41.8	1.2	1.9	1.9	0.0	0.0	0.0
4	25.1	25.8	25.7	48.1	46.2	46.3	2.2	3.3	3.3	0.0	0.0	0.0
5	16.2	17.5	17.5	51.4	48.4	48.5	3.8	5.6	5.5	0.0	0.0	0.0
6	9.1	10.8	10.7	51.8	47.8	48.1	6.9	9.1	8.9	0.0	0.1	0.1
7	4.6	6.3	6.2	48.1	44.3	44.6	11.7	13.7	13.5	0.1	0.2	0.2
8	2.2	3.5	3.4	41.2	38.5	38.7	17.9	19.1	19.0	0.2	0.4	0.4
9	1.0	1.8	1.8	32.7	31.3	31.4	24.5	24.6	24.6	0.4	0.9	0.8
10	0.4	0.9	0.8	23.9	23.6	23.6	30.7	29.7	29.8	0.9	1.7	1.6
11	0.2	0.4	0.3	15.3	16.0	15.9	35.9	33.6	33.8	1.9	3.3	3.2
12	0.0	0.1	0.1	8.3	9.6	9.5	38.3	34.9	35.2	4.1	6.0	5.8
13	0.0	0.0	0.0	4.3	5.6	5.4	36.9	33.3	33.6	7.3	9.6	9.4
14	0.0	0.0	0.0	2.2	3.0	2.9	32.9	29.4	29.7	11.2	13.9	13.7
15	0.0	0.0	0.0	1.1	1.5	1.5	27.7	24.0	24.4	15.4	18.7	18.4
16	0.0	0.0	0.0	0.6	0.7	0.7	22.3	18.2	18.6	19.1	23.1	22.7
17	0.0	0.0	0.0	0.3	0.3	0.3	17.2	12.7	13.1	22.1	26.6	26.1
18	0.0	0.0	0.0	0.2	0.1	0.1	12.7	8.3	8.7	24.0	28.4	28.0
19	0.0	0.0	0.0	0.1	0.1	0.1	9.0	5.3	5.6	24.8	28.6	28.2
20	0.0	0.0	0.0	0.0	0.0	0.0	6.2	3.3	3.6	24.5	27.4	27.1
21	0.0	0.0	0.0	0.0	0.0	0.0	4.1	2.1	2.2	23.1	25.2	25.0
22	0.0	0.0	0.0	0.0	0.0	0.0	2.3	1.1	1.2	20.4	21.6	21.5
23	0.0	0.0	0.0	0.0	0.0	0.0	1.2	0.5	0.6	16.5	17.1	17.1
24	0.0	0.0	0.0	0.0	0.0	0.0	0.6	0.2	0.3	12.5	12.8	12.8
25	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.1	0.1	8.9	9.0	9.0

a) Concentrations in mmol/L. Data computed for the mixtures listed in Table S3.

Table S4b. Calculated Phosphate Species Concentrations[a] at Equilibrium for the Series of Mixtures of Buffer Solution

Mix.	$[H_3PO_4]$			$[H_2PO_4^-]$			$[HPO_4^{2-}]$			$[PO_4^{3-}]$		
	$f = 1$	$b = 0.1$	$b = 0.2$	$f = 1$	$b = 0.1$	$b = 0.2$	$f = 1$	$b = 0.1$	$b = 0.2$	$f = 1$	$b = 0.1$	$b = 0.2$
1	4.3	4.2	4.2	17.5	17.6	17.6	0.0	0.0	0.0	0.0	0.0	0.0
2	4.0	4.0	4.0	27.7	27.7	27.7	0.0	0.0	0.0	0.0	0.0	0.0
3	3.4	3.5	3.4	37.7	37.6	37.6	0.0	0.0	0.0	0.0	0.0	0.0
4	2.6	2.8	2.8	46.8	46.6	46.6	0.0	0.0	0.0	0.0	0.0	0.0
5	1.9	2.1	2.1	55.1	54.8	54.9	0.0	0.0	0.0	0.0	0.0	0.0
6	1.2	1.5	1.5	63.2	62.8	62.9	0.0	0.0	0.0	0.0	0.0	0.0
7	0.7	1.1	1.0	70.2	69.9	69.9	0.1	0.1	0.1	0.0	0.0	0.0
8	0.4	0.7	0.7	76.5	76.2	76.2	0.1	0.1	0.1	0.0	0.0	0.0
9	0.3	0.5	0.5	82.3	82.1	82.1	0.2	0.2	0.2	0.0	0.0	0.0
10	0.2	0.3	0.3	87.6	87.5	87.5	0.4	0.4	0.4	0.0	0.0	0.0
11	0.1	0.2	0.2	92.6	92.6	92.6	0.8	0.7	0.7	0.0	0.0	0.0
12	0.1	0.1	0.1	97.0	97.2	97.2	1.6	1.3	1.3	0.0	0.0	0.0
13	0.0	0.1	0.1	99.9	100.8	100.7	3.1	2.1	2.2	0.0	0.0	0.0
14	0.0	0.1	0.1	101.8	103.6	103.4	5.4	3.6	3.7	0.0	0.0	0.0
15	0.0	0.0	0.0	102.7	105.6	105.3	8.8	5.9	6.1	0.0	0.0	0.0
16	0.0	0.0	0.0	102.4	106.4	106.0	13.5	9.6	10.0	0.0	0.0	0.0
17	0.0	0.0	0.0	100.8	105.3	104.9	20.1	15.5	16.0	0.0	0.0	0.0
18	0.0	0.0	0.0	97.6	102.0	101.6	28.7	24.3	24.7	0.0	0.0	0.0
19	0.0	0.0	0.0	92.6	96.3	96.0	39.6	35.9	36.2	0.0	0.0	0.0
20	0.0	0.0	0.0	86.0	88.9	88.6	52.5	49.6	49.9	0.0	0.0	0.0
21	0.0	0.0	0.0	77.6	79.7	79.5	67.9	65.8	66.0	0.0	0.0	0.0
22	0.0	0.0	0.0	65.9	67.1	67.0	88.6	87.4	87.5	0.0	0.0	0.0
23	0.0	0.0	0.0	51.8	52.4	52.4	112.9	112.3	112.3	0.0	0.0	0.0
24	0.0	0.0	0.0	38.6	38.9	38.9	135.3	135.0	135.0	0.0	0.0	0.0
25	0.0	0.0	0.0	27.2	27.4	27.3	154.5	154.3	154.3	0.0	0.0	0.0

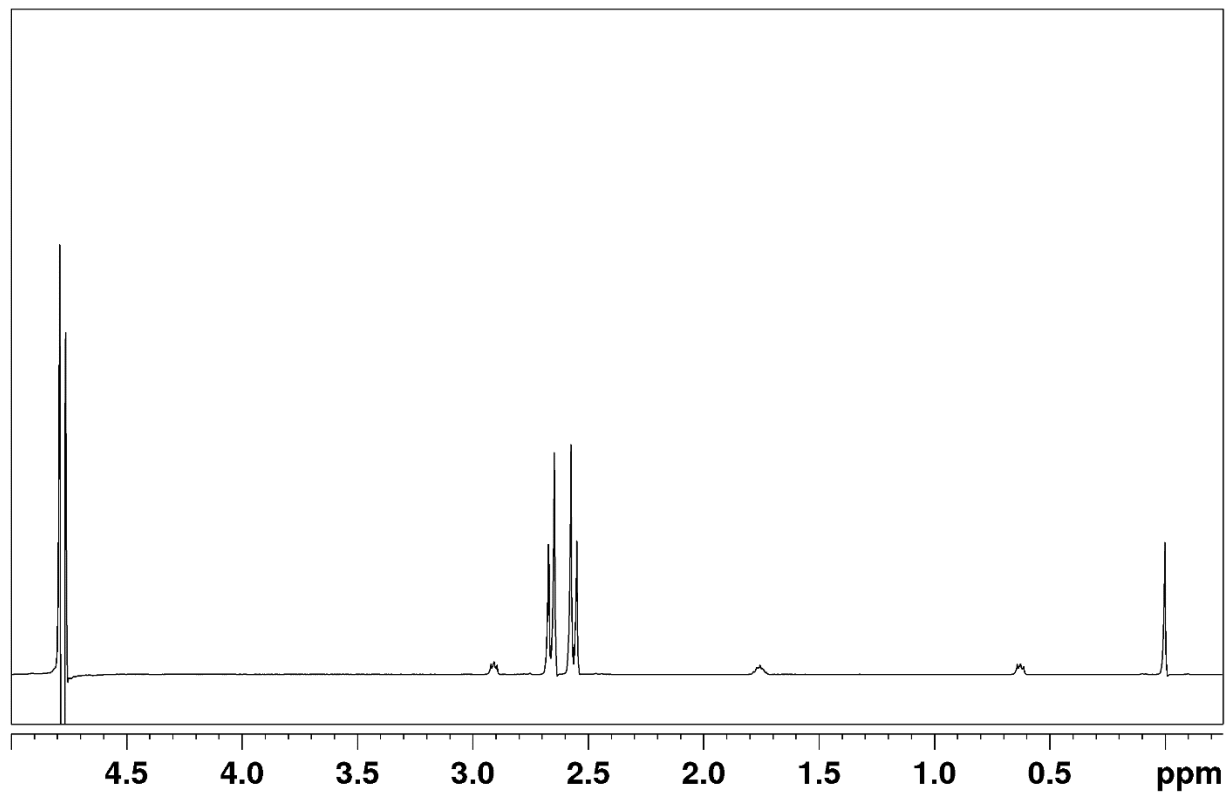a) Concentrations in mmol/L. Data computed for the mixtures listed in Table S3.

Figure S3. ^{1}H NMR spectrum of citric acid in 90% H_2O : 10% D_2O using a water suppression technique. The shifts for the citrate peak are given in Table S5 and the chemical shift of the water peak is 4.78 ppm.

Table S5. ^{1}H Chemical Shifts for Citric Acid in 90% H_2O : 10% D_2O (ppm relative to DSS)

pH	$\delta_H(A_1)$	$\delta_H(A_2)$	$\delta_H(B_1)$	$\delta_H(B_2)$
2.12	2.83	2.85	3.00	3.03
2.32	2.83	2.85	3.00	3.02
2.57	2.82	2.84	2.98	3.00
2.86	2.80	2.83	2.95	2.98
3.18	2.78	2.81	2.92	2.95
3.54	2.76	2.79	2.89	2.91
3.92	2.74	2.77	2.85	2.88
4.28	2.72	2.74	2.82	2.84
4.61	2.69	2.72	2.78	2.81
4.96	2.67	2.69	2.75	2.78
5.31	2.64	2.66	2.72	2.75
5.66	2.61	2.64	2.70	2.72
6.01	2.58	2.60	2.67	2.70
6.48	2.55	2.57	2.65	2.67
8.95	2.52	2.55	2.62	2.65