Supplementary data

Quantifying Hydrogel Response using Laser Light Scattering.

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General procedure for preparation of monobasic buffer solutions

The general method used to prepare monobasic buffers is detailed below, an example is included for the preparation of a 0.05 M ethanol amine buffer, at pH 10, using NaCl to fix the overall ionic strength to 0.1 M (prepared at 25°C).

Step 1: The pK_a of ethanol amine (9.50[1]) was thermodynamically adjusted for temperature and ionic strength using the Debye-Huckel relationship shown in equation 1,[2] where $\mathrm{p}K_{a^1}$ is the modified pK_a, z_a is the charge on the conjugate acid, I is the ionic strength of the solution and A is a constant which has a value of 0.5114 at 25 °C.[2]

$$\mathrm{p}K_{a^1} = \mathrm{p}K_a + (2z_a - 1)\cdot\left[\frac{A\sqrt{I}}{1+\sqrt{I}} - 0.1\cdot I\right] \quad \textbf{(1)}$$

$$\mathrm{p}K_{a^1} = 9.5 + ((2\times 0) - 1)\cdot\left[\frac{0.5114\sqrt{1.0}}{1+\sqrt{1.0}} - 0.1\times 1.0\right] \quad \textbf{(2)}$$

$$\mathrm{p}K_{a^1} = 9.61 \quad \textbf{(3)}$$

Step 2: The Henderson-Hasselbalch relationship (eq. 4) was then used to determine the concentration of base [A$^-$] and acid [HA] in the buffer at the given pH and the total buffer concentration (i.e. pH 10 at a total buffer concentration of 0.05M).

$$[\mathrm{pH}] = \mathrm{p}K_a + \log_{10}\frac{[\mathrm{A^-}]}{[\mathrm{HA}]} \quad \textbf{(4)}$$

Equation 4 implies that the acid component of the buffer is neutral, and the basic component has a negative charge. While this is true for many buffers, in the case of ethanol amine for example, the basic component is neutral and the acid component is charged (+1). For clarity the Henderson-Hasselbalch equation may be re-written as shown in equation 5, where A^-, defined as a proton acceptor from Bronsted-Lowry theory represents the base.

$$[\mathrm{pH}] = \mathrm{p}K_a + \log_{10}\frac{[\mathrm{base}]}{[\mathrm{acid}]} \quad \textbf{(5)}$$

The total concentration of acid and base in the buffer is given by equation 6.

$$C_{buffer} = [\mathrm{HA}] + [\mathrm{A^-}] \quad \textbf{(6)}$$

The concentration of acid [HA] is related to the concentration of hydrogen ion $[\mathrm{H^+}]$ and base $[\mathrm{A^-}]$ through the equilibrium constant, K_{a}, see equation 7.

$$[\mathrm{HA}] = \frac{[\mathrm{H^+}][\mathrm{A^-}]}{K_a} \quad \textbf{(7)}$$

Rearrangement, followed by substitution of equation 7 into 6 allows the concentration of base to be determined.

$$C_{buffer} = \frac{[\mathrm{H^+}][\mathrm{A^-}]}{K_a} + [\mathrm{A^-}] \quad \textbf{(8)}$$

$$[\mathrm{A^-}] = \frac{[C_{buf}]K_a}{K_a + [\mathrm{H^+}]} \quad \textbf{(9)}$$

$$[\mathrm{A^-}] = \frac{[0.05][2.45\times10^{-10}]}{[2.45\times10^{-10}] + [1\times10^{-10}]} \quad \textbf{(10)}$$

$$[\mathrm{A^-}] = 0.0354\mathrm{M} \quad \textbf{(11)}$$

$$[\mathrm{HA}] + [\mathrm{A^-}] = 0.05\mathrm{M} \quad \textbf{(12)}$$

$$[\mathrm{HA}] = 0.0146\ \mathrm{M} \quad \textbf{(13)}$$

Step 3: Using this information the ionic strength of the buffer species can then be determined.

The ionic strength describes the overall ionic properties of the solution. It is a function of the concentration of all individual species dissolved in solution; encompassed in equation 14.

$$I = \frac{1}{2}\sum_{i=1}^{n}(c_i z_i^2) \tag{14}$$

where c_i is the concentration of the ionic species, i, and z_i is the charge on that ion. The total ionic strength is taken as the sum of all species.

In this example the concentration of [base] and [acid] is 0.0354 M and 0.0146 M, respectively.

The final buffer can be prepared in 2 ways (1) by dissolving the required amount of basic and acidic components in solution to give a final solution at the correct pH, (2) dissolve the required amount of basic or acid component in solution, then titrate it to the required pH using either strong acid or base.

In the case of citric acid buffer, the only ions which contribute to the ionic strength are protonated ethanol amine ($HOCH_2NH_3^+$) and chloride anion (Cl^-).

There ionic strength is calculated below,

$$I = \frac{1}{2}(\mathrm{HOCH_2NH_3}^{+} \times 1^2) + (\mathrm{Cl}^{-} \times \text{-}1^2) \tag{15}$$

$$I = \frac{1}{2}(0.0146 \times 1^2) + (0.0146 \times -1^2) \tag{16}$$

$$I = 0.015\,\mathrm{M} \tag{17}$$

As, $I_{total} = I_{buffer} + I_{salt}$, **(18)**

where I_{buffer} and I_{salt} are the ionic strength due to the added salt and buffer species acting alone, respectively. This indicates that another 0.085 M of NaCl must be added to maintain an ionic strength of 0.1 M

General procedure for preparation of multivalent buffer solutions

The method used to prepare multivalent buffers is more complicated. A full derivation will not be given here but the following equations describe the general principles.

Equations (19-23) describe how the fractional composition of each ionic species (H_3A, H_2A^- and A_3^-) in a trivalent buffer, such as citric acid used in this study, vary with changes in pK_a, (thermodynamically corrected), the total concentration of hydronium ion given by D, and the total buffer concentration [C].[3]

The fractional composition of each species multiplied by the total buffer concentration [C] gives the concentration of each species in solution (mol dm^{-3}). The concentration of each individual species can then be inserted into equation 14, to give the ionic strength. Summation of the ionic strength for each species gives I_{buffer} (equation 18). From I_{buffer} one can determine the amount of salt that must be added to maintain a fixed ionic strength. Care must be taken to use the correct charge and include all the counterions.

$$K = \mathrm{D}^3 + \mathrm{D}^2 K_{a1} + \mathrm{D} K_{a1} K_{a2} + K_{a1} K_{a2} K_{a3} \tag{19}$$

$$f(\mathrm{H_3A}) = \frac{[\mathrm{H_3A}]}{C} = \frac{\mathrm{D}^3}{K} \tag{20}$$

$$f(\mathrm{H_2A^-}) = \frac{[\mathrm{H_2A^-}]}{C} = \frac{\mathrm{D}^2 K_{a1}}{K} \tag{21}$$

$$f(\mathrm{HA^{2-}}) = \frac{[\mathrm{HA^{2-}}]}{C} = \frac{\mathrm{D} K_{a1} K_{a2}}{K} \tag{22}$$

$$f(\mathrm{A^{3-}}) = \frac{[\mathrm{A^{3-}}]}{C} = \frac{K_{a1} K_{a2} K_{a3}}{K} \tag{23}$$

Buffer recipe used to measure the effect of salt identity on the "static" response of the diffraction grating

Table 1. Amount of citric acid and added salt required to maintain a fixed buffering capacity and ionic strength in a 100 mL solution.

Salt	NaAce	NaCl	$NaNO_3$	NaBr	NaI	NaSCN
pH	3.6	3.6	3.6	3.6	3.6	3.6
Concentration of buffer required/ M	0.01	0.01	0.01	0.01	0.01	0.01
Ionic strength of buffer due to buffer species alone/ M	0.01	0.01	0.01	0.01	0.01	0.01
Required Ionic Strength/ M	0.1	0.1	0.1	0.1	0.1	0.1
Amount of citric acid/ g	1.92	1.92	1.92	1.92	1.92	1.92
Amount of added salt/ g	0.74	0.52	0.76	0.92	1.34	0.73

Buffer recipe used to measure the "dynamic" response of the diffraction grating

Table 2. Amount of buffer and NaCl required to maintain a fixed buffering capacity and ionic strength in a 100 mL solution.

Buffer	Ethanol amine	Citric acid
pH	11.2	3.6
Concentration of buffer required/ M	0.05	0.05
Ionic strength of buffer due to buffer species alone/ M	0.0013	0.05
Required Ionic Strength/ M	0.1	0.1
Amount of buffer/ g	0.31	0.96
Amount of NaCl/ g	0.60	0.28

References

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2. R. J. Beynon and J. S. Easterby, *Buffer Solutions*, IRL Press, New York, 1996.
3. P Atkins and J d. Paula, *Elements of Physical Chemistry, 3 ed,* Oxford University Press, Oxford , 2000.