

INTRODUCTION

Slight variations in the pH of the mobile phase at a pH near the analyte pK_a can result in significant changes in retention times

$$t_R = \frac{t_{R(A)} + t_{R(HA)} 10^{\frac{s}{w} pK_a - \frac{s}{w} pH}}{1 + 10^{\frac{s}{w} pK_a - \frac{s}{w} pH}}$$

t_R → retention time of the ionisable analyte
 $t_{R(HA)}$ → retention time of the acidic species
 $t_{R(A)}$ → retention time of the basic species
 pK_a → dissociation constant of the analyte in the mobile phase
 pH → pH of the mobile phase

pH VARIATION OF THE BUFFER

Linear relations

$$\frac{s}{w} pH = \frac{w}{w} pH + m_{pH} \phi_{MeCN}$$

$\frac{s}{w} pH$ → pH measured in MeCN-water with electrodes calibrated in water

$\frac{w}{w} pH$ → pH measured in the aqueous buffer

ϕ_{MeCN} → volume fraction of MeCN

m_{pH} → depends on
 the particular buffering system used
 the aqueous pH value
 the concentration of the aqueous buffer
 before adding MeCN

pK_a values of the buffering species

$$\frac{s}{w} pK_a = \frac{w}{w} pK_a + m_{pK} \phi_{MeCN}$$

Buffering system	0%	20%	40%	60%	m_{pK}
Formic acid	3.79	4.03	4.44	4.90	1.76
Piperazine (pK_{a1})	5.37	5.26	5.19	5.06	-0.50
Piperazine (pK_{a2})	9.76	9.62	9.53	9.42	-0.58
Tris	8.08	7.94	7.85	7.72	-0.59
Boric acid	9.23	9.85	10.43	11.00	2.98
Hydrogencarbonate	10.35	10.82	11.31	11.62	2.20

Acetonitrile content in volume, zero ionic strength, 25°C

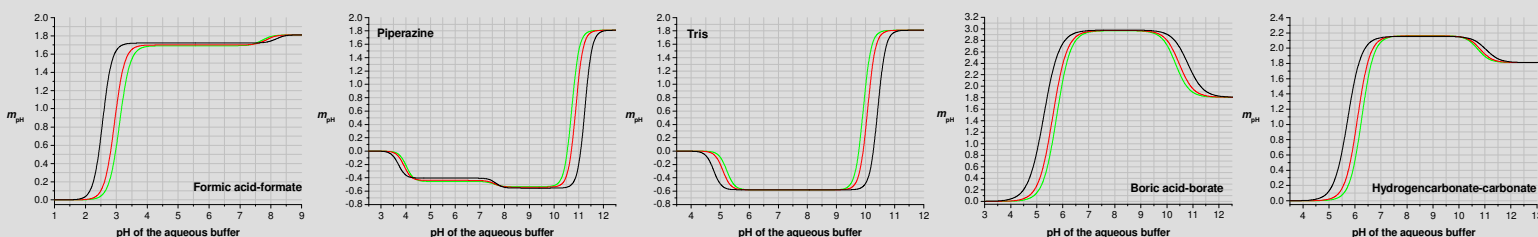


Figure 1. Variation of the m_{pH} slope with the initial aqueous pH of the buffer before adding the organic modifier. Green line represents aqueous buffer concentration of $0.005 \text{ mol}\cdot\text{L}^{-1}$, red line $0.01 \text{ mol}\cdot\text{L}^{-1}$, and black line $0.05 \text{ mol}\cdot\text{L}^{-1}$.

$$m_{pH} = \frac{a_0 + \sum_{i=1}^n a_i 10^{s(i \frac{w}{w} pH - b_i)} + a_{n+1} 10^{s((n+1) \frac{w}{w} pH - b_{n+1})}}{1 + \sum_{i=1}^n 10^{s(i \frac{w}{w} pH - b_i)} + 10^{s((n+1) \frac{w}{w} pH - b_{n+1})}}$$

s depend on the buffer used and on the initial aqueous concentration of the buffer
 a_i
 b_i

n number of acid-base equilibria

Linear variation of the s , a_i and b_i parameters for the studied buffers depending on the aqueous buffer concentration, c_T ($0.001 < c_T < 0.1 \text{ mol}\cdot\text{L}^{-1}$)

Parameter	Formic acid	Piperazine	Tris	Boric acid	Hydrogencarbonate
s	$0.37 \log c_T + 3.49$	$0.11 \log c_T + 3.25$	$0.02 \log c_T + 3.41$	$-0.20 \log c_T + 1.21$	$-0.24 \log c_T + 1.36$
a_0	0.00	0.00	0.00	0.00	0.00
a_1	$0.03 \log c_T + 1.76$	$0.05 \log c_T - 0.34$	-0.58	$0.01 \log c_T + 2.99$	$-0.01 \log c_T + 2.14$
a_2	1.81	$-0.02 \log c_T - 0.58$	1.81	1.81	1.81
a_3	-	1.81	-	-	-
b_1	$-0.55 \log c_T + 1.84$	$-0.32 \log c_T + 3.29$	$-0.45 \log c_T + 4.19$	$-0.50 \log c_T + 4.62$	$-0.54 \log c_T + 5.02$
$b_2 - b_1$	$0.45 \log c_T + 8.75$	$0.06 \log c_T + 7.72$	$0.50 \log c_T + 11.06$	$0.47 \log c_T + 11.42$	$0.32 \log c_T + 11.46$
$b_3 - b_2$	-	$0.53 \log c_T + 11.94$	-	-	-

BUFFER CAPACITY

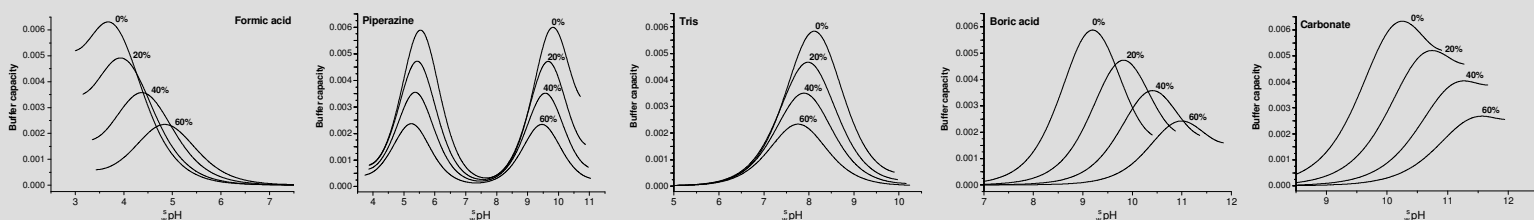


Figure 2. Buffer capacity variation of the studied buffers at 0, 20, 40 and 60% (v/v) acetonitrile-water compositions. Initial aqueous buffer concentration of $0.01 \text{ mol}\cdot\text{L}^{-1}$.

- ✓ Maximum buffer capacities are achieved when the pH of the solution is equal to the pK_a of the buffering species in the particular solvent composition at the working ionic strength
- ✓ Good buffer capacities are obtained in the pH range included between 1 pH unit below and above the pK_a value of the buffer

REFERENCES

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