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**METAL BUFFERS IN
CHEMICAL ANALYSIS: PART I –
THEORETICAL CONSIDERATIONS**

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Metal buffers in chemical analysis: Part I — Theoretical considerations

Abstract - A theoretical treatment of metal buffers in single and two phase systems is given. Equations are derived for the relationship between the pM-value on one hand, and the stability products of the complexes formed between the metal ions and the complexing ligands, as well as the pH of the solutions on the other hand. Examples are given for the use of the equations. Relevant data are given in tabulated form to aid potential users in the choice of suitable metal buffer systems.

1. INTRODUCTION

The aim of the present discussion is to endeavor to achieve a better and wider acceptance of the use of metal buffers, especially in chemical analysis.

By analogy with the definition of a pH-buffer, which is a solution for which the pH-value is only slightly affected by dilution or by the addition of a relatively small amount of a strong acid or strong base, a metal buffer solution can be defined as a solution for which the pM-value is only slightly affected by the addition of a metal ion (M) or a ligand (L) which complexes with the metal ion. Normally, the pM-value would also be almost independent of dilution. Such solutions cannot strictly be considered metal buffers, but do allow preparation of a solution of a particular pM-value, e.g., for calibration purposes, and thus have been included in this review.

Buffer regions in acid-base titration curves (pH vs. added titrant) can be recognized as the regions of low slope along these curves. Similarly pM buffer action occurs in the almost horizontal regions in the titration curves, that is, pM vs. fraction of metal ions titrated (f) with a ligand. When we consider a simple titration curve of a metal ion with a ligand forming 1:1 complexes with the metal ion, two parts in the titration curve can be considered as buffer regions: the first, right from the start of the titration ($f < 0.7$) and the second after the equivalence point ($f > 1.3$). These buffer regions are shown in Fig. 1.

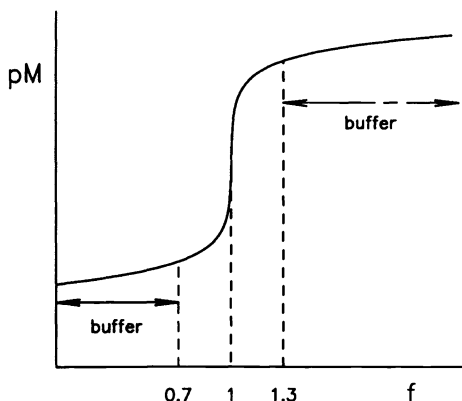


Fig. 1. Titration curve when a metal ion M is titrated with a ligand L forming the complex ML. $f = C(L)/C(M)$. Buffer regions are marked in the figure.

It should be noted that the total analytical concentration of the metal ion ($C(M)$) should not be low as otherwise the addition of a small amount of metal ion or ligand may correspond to a large change in the value of f . This means that solutions of metal ions of not too low concentration can be used as pM buffers, as is the case for solutions for pH buffers.

The real problem with metal buffers, as with pH buffers, is to be able to prepare buffers with high pM-values. As can be seen from the titration curve, such buffers can be prepared by adding an excess of a chelating agent to a solution of the metal ion. As the chelating agents very often are anions of polyprotic acids, the solution also has to be buffered for pH. In the following sections the theory of metal buffers, their preparation and their applications will be outlined.

2. SINGLE PHASE SYSTEMS

2.1. Theoretical aspects of calculation of pM-values

Conditional constants and side-reaction coefficients. When a metal buffer solution is to be prepared it is often best to choose a chelating agent which reacts with the metal ion in the ratio 1:1. If, for some reason this ratio is not 1:1, the equilibrium equations will be more complicated, particularly when polynuclear complexes are formed. In this section the discussion will be restricted to 1:1 mononuclear complex formation.

When a metal ion and a ligand react, the following equations apply, at constant ionic strength:

$$C(M) = [M] + [ML] \quad (1)$$

$$C(L) = [L] + [ML] \quad (2)$$

$$K_{ML} = [ML]/([M][L]) \quad (3)$$

where $C(M)$ and $C(L)$ are the total analytical concentrations of the metal and the ligand in the solution and K_{ML} is the stability constant for the complex.

If the reactants participate in side-reactions, for example with hydrogen or hydroxide ions, the equilibrium calculations can be performed according to Ringbom (ref. 1), using a conditional constant defined by

$$K_{(ML)'}^{M',L'} = [(ML)'] / ([M'] [L']) \quad (4)$$

where $[(ML)']$ is the sum of concentrations of all species containing M and L in the mole ratio 1:1, that is,

$$[(ML)'] = [ML] + [HML] + [(OH)ML] + \dots \quad (5)$$

$[M']$ denotes the concentration not only of the free metal ion but also of all the metal in solution that has not reacted with the complexing agent, that is,

$$[M'] = [M] + [MOH] + [M(OH)_2] + \dots \quad (6)$$

In a corresponding manner, $[L']$ represents not only the concentration of the free ligand but also the concentrations of all species of the complexing agent not bound to the metal, that is,

$$[L'] = [L] + [HL] + [H_2L] + \dots \quad (7)$$

Using the side-reaction coefficients α_{ML} , α_M and α_L , defined by

$$\alpha_{ML} = [(ML)'] / [ML] \quad (8)$$

$$\alpha_M = [M'] / [M] \quad (9)$$

$$\alpha_L = [L'] / [L] \quad (10)$$

which take into consideration the different side-reactions, the conditional constant can be written

$$K_{(ML)'}^{M',L'} = \alpha_{ML} K_{ML} / (\alpha_M \alpha_L) \quad (11)$$

The different side-reaction coefficients can be calculated from known stability constants using the equation

$$\alpha_{X(Y)} = 1 + [Y] \beta(X,Y) + [Y]^2 \beta(X,2Y) + \dots + [Y]^n \beta(X,nY) \quad (12)$$

where

$$\beta(X,nY) = [XY_n] / ([X][Y]^n) \quad (13)$$

If the only interfering ion forming various complexes with the complexing agent is the hydrogen ion, that is, $X = L$ and $Y = H$ in equation (12), the side-reaction coefficient α_L is

$$\alpha_{L(H)} = 1 + [H] \beta(L,H) + [H]^2 \beta(L,2H) + \dots + [H]^n \beta(L,nH) \quad (14)$$

and

$$\beta(L,nH) = [H_n L] / ([H]^n [L]) \quad (15)$$

where n can be a number between 1 and ν if the polybasic acid is $H_\nu L$.

From equation (11) it follows that

$$pM' = \log K_{ML} - \log \alpha_M + \log(\alpha_{ML}/\alpha_L) + \log([L']/[(ML)']) \quad (16)$$

which also can be written

$$pM = \log K_{ML} + \log(\alpha_{ML}/\alpha_L) + \log([L']/[(ML)']) \quad (17)$$

From equation (17) it is clear that three terms can be varied to achieve a desired pM-value:

- The first term ($\log K_{ML}$) is of great importance; a proper selection of the ligand forming a complex of proper stability ($\log K_{ML} > 7$) is the first step in the selection of materials for the preparation of a metal buffer.
- The second term ($\log(\alpha_{ML}/\alpha_L)$) provides great flexibility to adjust pM, especially by means of α_L . As is well known, α_L is strongly dependent on pH, if the chelating agent is a polyprotic acid. Hence selection of an appropriate pH-value may result in the desired pM-value.
- As to the last term ($\log([L']/[(ML)'])$), as mentioned in the introduction, this ratio should correspond to a point in the titration curve at some distance after the equivalence point, that is, $f > 1$. It is useful to note that unless very large excesses of the ligand are used, this term does not affect the pM-value very much. When the ratio $[L']/[(ML)'] = 1$, which means a titration of M with L to a 100 % over-titration situation, the last term vanishes.

As values of the conditional constant as a function of pH have been tabulated (ref. 1,2) it is important to know if the values include also α_M . A fast check can be made using Table 1, in which values of $\log \alpha_{M(OH)}$ are tabulated as functions of pH.

If the $\log \alpha_{M(OH)}$ -value is larger than unity in value, the metal ion takes part in a side-reaction with hydroxide ions. This side-reaction has been taken into account when the conditional constants (ref. 1) at different pH-values are calculated and tabulated. In Table 2 logarithmic conditional constants of metal-EDTA, metal-EGTA and metal-DCTA complexes are given. A glance at Table 1 shows immediately if $\log \alpha_{M(OH)}$ must be taken into account when a pM-value is calculated using the values in Table 2. If a pM'-value has been calculated using a conditional constant, it can be converted into a pM-value using

$$pM = pM' + \log \alpha_{M(OH)} \quad (18)$$

For example, the logarithmic conditional constant of the Zn-EDTA complex at pH = 10 is 13.59 (Table 2). From Table 1 the logarithmic value of the side-reaction coefficient is 2.41. This value indicates that the side-reaction coefficient $\alpha_{M(OH)}$ has been taken into account when the conditional constant of the Zn-EDTA complex is calculated.

The use of the data in Tables 1 and 2 will be illustrated in the following examples.

Example 1. A copper buffer was prepared according to the following procedure: To 50.00 mL of an 0.010 M copper nitrate solution was added 50.00 mL of an 0.020 M EGTA solution and the pH was adjusted to 8. The pCu-value is calculated as follows:

From Table 1 is found that $\log \alpha_{Cu(OH)} = 0.3$, and from Table 2 that the logarithmic value of the conditional constant is 14.89.

Since $[CuL] = [L'] = 0.005$ M, substituting the values into equation (16) gives

$pCu' = 14.89$ and thus (using equation (18))

$pCu = 14.89 + 0.3 = 15.19$.

Table 1. Logarithmic Values of $\alpha_{M(OH)}$ for Various Metals as Functions of pH.

| Metal | pH | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 |
|---------|----|------|------|------|------|------|------|------|-------|-------|-------|-------|-------|-------|
| Ag | | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | 0.08 | 0.54 | 2.09 | 4.83 |
| Al | | 0.00 | 0.00 | 0.00 | 0.00 | 1.32 | 5.30 | 9.30 | 13.30 | 17.30 | 21.30 | 25.30 | 29.30 | 33.30 |
| Ba | | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.02 | 0.18 | 0.78 |
| Ca | | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | 0.08 | 0.48 | 1.32 |
| Cd | | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | 0.08 | 0.55 | 1.96 | 4.55 | 8.08 | 12.01 |
| Co(II) | | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | 0.05 | 0.35 | 1.13 | 2.15 | 4.23 | 7.20 | 10.20 |
| Cu | | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.04 | 0.30 | 1.04 | 2.00 | 3.00 | 4.00 | 5.00 | 6.00 |
| Fe(II) | | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | 0.12 | 0.62 | 1.51 | 2.50 | 3.50 | 4.50 |
| Fe(III) | | 0.04 | 0.40 | 1.79 | 3.71 | 5.70 | 7.70 | 9.70 | 11.70 | 13.70 | 15.70 | 17.70 | 19.70 | 21.70 |
| Hg | | 0.01 | 0.23 | 1.73 | 3.70 | 5.70 | 7.70 | 9.70 | 11.70 | 13.70 | 15.70 | 17.70 | 19.70 | 21.70 |
| Mg | | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.02 | 0.15 | 0.70 | 1.61 | 2.60 |
| Mn(II) | | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | 0.10 | 0.55 | 1.42 | 2.40 | 3.40 |
| Ni | | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.02 | 0.15 | 0.70 | 1.61 | 2.60 | 3.60 | 4.60 |
| Pb | | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | 0.06 | 0.42 | 1.28 | 2.58 | 4.62 | 7.34 | 10.30 | 13.30 |
| Sr | | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.03 | 0.21 | 0.86 |
| Zn | | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | 0.18 | 2.41 | 5.41 | 8.45 | 11.75 | 15.53 |

Example 2. To a solution 0.050 M in a zinc salt and 0.080 M in EDTA was added a noncomplexing pH buffer to adjust the pH to 9. The pZn is calculated as follows:

From Table 1 the value of the logarithmic side-reaction coefficient is found to be 0.18, and from Table 2 the corresponding value of the logarithmic conditional constant is 14.96.

Since $[L'] = 0.030 \text{ M}$ and $[ZnL] = 0.050 \text{ M}$, equation (16) gives

$$pZn' = 14.96 + \log(0.030/0.050) = 14.74, \text{ and thus}$$

$$pZn = 14.74 + 0.18 = 14.92.$$

As already mentioned, the principal way of influencing the pM-value of a solution containing a given complexing agent is by adjusting the term $\log(\alpha_{ML}/\alpha_L)$ in equation (17). The usual way to accomplish this is by adjusting the pH of the solution, thus changing the value of $\alpha_{L(H)}$. One advantage of this method is of course that the pH of the solution can readily be measured with good accuracy. The data in Example 3 illustrates how the pHg-value in a Hg-EDTA solution will change with pH.

Example 3. A solution was 0.010 M in a mercury(II) salt and 0.020 M in EDTA. The pHg-value is to be calculated for the following pH-values: 4, 5, 6, 7 and 8.

The following Table, in which values from Tables 1 and 2 have been collected, illustrates the method of calculation. Since the concentration of the Hg-EDTA complex equals the concentration of the free ligand, the logarithmic value of the conditional constant represent also the pHg'-value.

| pH | 4 | 5 | 6 | 7 | 8 | |
|--------------------------|-------|-------|-------|-------|-------|---------|
| $\log K_{HgL}^{Hg', L'}$ | 11.42 | 11.40 | 11.22 | 10.59 | 9.68 | (=pHg') |
| $\log \alpha_{Hg(OH)}$ | 1.73 | 3.70 | 5.70 | 7.70 | 9.70 | |
| pHg | 13.15 | 15.10 | 16.92 | 18.29 | 19.38 | |

Table 2. Logarithmic Conditional Constants of Metal-EDTA, Metal-EGTA and Metal-DCTA Complexes. (The values are based on tabulated stability constants (see ref. 10); they are approximately valid at $I = 0.1 \text{ M.}$)

| Metal | | pH 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 |
|------------------|------|------|------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Ag | EDTA | | | | | | 1.75 | 2.84 | 3.95 | 4.97 | 5.96 | 6.81 | 7.15 | 6.77 | 5.23 | |
| | EGTA | | | | | | | | 2.41 | 4.36 | 6.01 | 6.73 | 6.78 | 6.34 | 4.79 | |
| | DCTA | | | | | | | 2.84 | 4.19 | 5.24 | 6.25 | 7.33 | 8.10 | 8.29 | 6.91 | |
| Al | EDTA | | 3.22 | 5.63 | 7.71 | 9.75 | 10.56 | 8.72 | 6.75 | 4.74 | | | | | | |
| | EGTA | | | | 2.27 | 3.72 | 5.67 | 6.97 | 5.93 | 4.88 | 3.53 | | | | | |
| | DCTA | | 3.59 | 6.76 | 9.37 | 11.48 | 12.00 | 9.45 | 6.96 | 4.84 | | | | | | |
| Ba | EDTA | | | | | | | 3.10 | 4.45 | 5.51 | 6.50 | 7.36 | 7.77 | 7.83 | 7.68 | 7.08 |
| | EGTA | | | | | | | 2.04 | 3.95 | 5.89 | 7.54 | 8.27 | 8.39 | 8.39 | 8.23 | 7.63 |
| | DCTA | | | | | | 2.38 | 3.28 | 4.02 | 4.92 | 5.91 | 6.90 | 7.84 | 8.46 | 8.49 | 7.91 |
| Ca | EDTA | | | | 2.06 | 4.01 | 5.83 | 7.20 | 8.26 | 9.23 | 10.11 | 10.52 | 10.52 | 10.13 | 9.29 | |
| | EGTA | | | | | 2.52 | 4.50 | 6.50 | 8.45 | 10.10 | 10.83 | 10.95 | 10.89 | 10.49 | 9.65 | |
| | DCTA | | | | 3.07 | 5.18 | 7.01 | 8.36 | 9.41 | 10.42 | 11.41 | 12.34 | 12.92 | 12.70 | 11.88 | |
| Cd | EDTA | | 3.71 | 5.92 | 7.89 | 9.86 | 11.68 | 13.05 | 14.10 | 15.02 | 15.41 | 14.41 | 11.90 | 8.38 | 4.45 | |
| | EGTA | | 2.64 | 4.64 | 6.33 | 8.24 | 10.23 | 12.22 | 14.17 | 15.75 | 16.02 | 14.72 | 12.15 | 8.62 | 4.69 | |
| | DCTA | | 4.76 | 7.45 | 9.84 | 11.91 | 13.74 | 15.09 | 16.13 | 17.07 | 17.60 | 17.12 | 15.18 | 11.82 | 7.92 | |
| Co ²⁺ | EDTA | | 3.74 | 5.87 | 7.76 | 9.71 | 11.53 | 12.89 | 13.91 | 14.60 | 14.67 | 14.07 | 12.07 | | | |
| | EGTA | | | | 2.94 | 4.22 | 5.96 | 7.91 | 9.82 | 11.17 | 11.12 | 10.22 | 8.16 | | | |
| | DCTA | | 4.36 | 7.10 | 9.52 | 11.60 | 13.43 | 14.77 | 15.78 | 16.48 | 16.80 | 16.62 | 15.18 | | | |
| Cu ²⁺ | EDTA | | 3.37 | 6.14 | 8.31 | 10.23 | 12.20 | 14.02 | 15.35 | 16.15 | 16.40 | 16.31 | 15.83 | 15.41 | 15.31 | 15.30 |
| | EGTA | | | 4.53 | 6.45 | 7.76 | 9.33 | 11.25 | 13.19 | 14.89 | 15.80 | 15.57 | 14.69 | 13.71 | 12.71 | 11.71 |
| | DCTA | | 4.00 | 6.92 | 9.58 | 11.92 | 13.98 | 15.80 | 17.11 | 17.91 | 18.18 | 18.21 | 18.15 | 17.81 | 17.09 | 16.62 |
| Fe ²⁺ | EDTA | | | 3.74 | 5.74 | 7.72 | 9.54 | 10.91 | 11.97 | 12.96 | 13.82 | 14.22 | 14.19 | 13.70 | 12.81 | |
| | EGTA | | | | | 3.52 | 5.41 | 7.40 | 9.35 | 11.00 | 11.73 | 11.84 | 11.75 | 11.25 | 10.36 | |
| | DCTA | | | 2.69 | 6.12 | 8.77 | 10.88 | 12.71 | 14.06 | 15.11 | 16.12 | 17.11 | 18.04 | 18.58 | 18.26 | 17.38 |
| Fe ³⁺ | EDTA | 5.11 | 8.21 | 11.45 | 13.92 | 14.71 | 14.79 | 14.64 | 14.11 | 13.68 | 13.67 | 14.02 | | | | |
| | EGTA | | | 4.88 | 7.43 | 8.22 | 8.32 | 8.33 | 8.32 | 8.28 | 7.93 | 6.66 | | | | |
| | DCTA | 6.01 | 9.99 | 13.85 | 16.92 | 18.18 | 18.37 | 18.21 | 17.56 | 16.63 | 15.80 | 15.39 | | | | |
| Hg ²⁺ | EDTA | 3.40 | 6.37 | 9.12 | 11.03 | 11.42 | 11.40 | 11.22 | 10.59 | 9.68 | 8.89 | 8.45 | 7.82 | 6.89 | 5.90 | 4.90 |
| | EGTA | 2.92 | 5.89 | 8.65 | 10.60 | 11.02 | 11.03 | 11.02 | 10.98 | 10.63 | 9.36 | 7.49 | 5.50 | 3.50 | 1.50 | |
| | DCTA | 4.01 | 7.00 | 9.91 | 12.35 | 13.19 | 13.28 | 13.11 | 12.46 | 11.51 | 10.53 | 9.63 | 9.07 | 8.61 | 7.78 | 6.80 |
| Mg | EDTA | | | | | | 2.22 | 4.02 | 5.38 | 6.44 | 7.43 | 8.27 | 8.56 | 8.08 | 7.18 | |
| | EGTA | | | | | | | | 1.51 | 2.87 | 4.36 | 5.06 | 5.05 | 4.51 | 3.60 | |
| | DCTA | | | | | | 3.00 | 4.83 | 6.18 | 7.23 | 8.24 | 9.22 | 10.03 | 10.12 | 9.38 | |
| Mn ²⁺ | EDTA | | | 3.43 | 5.32 | 7.27 | 9.09 | 10.46 | 11.52 | 12.50 | 13.27 | 13.24 | 12.44 | 11.47 | 10.47 | |
| | EGTA | | | | 2.83 | 4.11 | 5.85 | 7.81 | 9.76 | 11.40 | 12.04 | 11.72 | 10.86 | 9.88 | 8.88 | |
| | DCTA | | | 2.13 | 4.92 | 7.38 | 9.46 | 11.29 | 12.64 | 13.69 | 14.69 | 15.60 | 16.09 | 15.86 | 15.05 | 14.08 |
| Ni | EDTA | | 3.39 | 6.14 | 8.24 | 10.08 | 12.02 | 13.84 | 15.21 | 16.25 | 17.11 | 17.42 | 16.92 | | | |
| | EGTA | | | | 3.88 | 5.06 | 6.12 | 7.38 | 9.11 | 11.02 | 12.53 | 12.71 | 11.92 | | | |
| | DCTA | | | 3.28 | 6.71 | 9.36 | 11.47 | 13.30 | 14.64 | 15.69 | 16.56 | 17.01 | 17.03 | | | |
| Pb | EDTA | | 2.41 | 5.20 | 7.46 | 9.46 | 11.44 | 13.26 | 14.57 | 15.27 | 15.40 | 14.96 | 13.34 | 10.69 | 7.73 | 4.74 |
| | EGTA | | | 2.43 | 4.34 | 5.54 | 6.71 | 8.31 | 10.18 | 11.78 | 12.56 | 11.99 | 10.08 | 7.37 | 4.41 | |
| | DCTA | | 2.08 | 5.03 | 7.82 | 10.28 | 12.36 | 14.18 | 15.47 | 16.18 | 16.32 | 16.03 | 14.92 | 12.83 | 10.05 | 7.08 |
| Sr | EDTA | | | | | | 2.16 | 3.96 | 5.32 | 6.38 | 7.37 | 8.23 | 8.64 | 8.69 | 8.52 | 7.87 |
| | EGTA | | | | | | | 2.13 | 4.04 | 5.98 | 7.63 | 8.36 | 8.48 | 8.47 | 8.29 | 7.64 |
| | DCTA | | | | | | 2.57 | 4.40 | 5.75 | 6.80 | 7.81 | 8.80 | 9.74 | 10.36 | 10.35 | 9.72 |
| Zn | EDTA | | 3.84 | 6.01 | 7.94 | 9.90 | 11.72 | 13.09 | 14.14 | 14.96 | 13.59 | 11.05 | 8.34 | 5.79 | 2.97 | |
| | EGTA | | | | 2.23 | 3.43 | 4.64 | 6.29 | 8.23 | 10.17 | 11.65 | 10.15 | 7.28 | 4.25 | | |
| | DCTA | | | 4.20 | 6.89 | 9.28 | 11.35 | 13.18 | 14.53 | 15.57 | 16.41 | 15.18 | 13.12 | 10.71 | 7.59 | 3.83 |

There is, however, an alternative way of influencing the side-reaction coefficient α_L and consequently the pM-value. If another metal ion N - having a stability constant K_{NL} which is much smaller than K_{ML} , but such that $\alpha_{L(N)} \gg \alpha_{L(H)}$ - is present in the solution, the titration curve $pM = f(f)$ will show two pM jumps as illustrated in Fig. 2. The shape of the titration curve will depend on the total analytical concentrations of the metal ions ($C(M)$ and $C(N)$) and on the stability constants K_{ML} and K_{NL} .

The curves in Fig. 2 can be calculated using, besides equations (1) and (3), the following:

$$C(N) = [N] + [NL] \quad (19)$$

$$C(L) = [L] + [ML] + [NL] \quad (20)$$

$$K_{NL} = [NL]/([N][L]) \quad (21)$$

$$f = C(L)/C(M) \quad (22)$$

$$[M] = C(M)/(1 + [L]K_{ML}) \quad (23)$$

In contrast to the titration curve shown in Fig. 1, which contains two buffer regions, the titration curve in Fig. 2 also shows a new, third buffer region, which is located between the two equivalence points. The first equivalence point (pM_{eq1}) occurs when $C(L) = C(M)$, and the second (pM_{eq2}) when $C(L) = C(M) + C(N)$. The two equivalence points are marked in Fig. 2, with (x), for the example when $C(M) = C(N)$.

From Fig. 2 can be seen that the concentration of the second metal (N) in the solution must preferably be higher than ca 0.5 $C(M)$ before the buffer region is large enough to be useful in practice. Normally a useful region is obtained if $C(N) > C(M)$.

Depending on the stability constant of the second metal (K_{NL}) the pM-value can be varied by choice of an appropriate second metal. In Fig. 3 the pM-values for different values of K_{NL} are shown as functions of the fraction titrated. The curve for $\log K_{NL} = 5$ is the same as the curve in Fig. 2 for $C(M) = C(N)$. Inspection of the two figures shows how a buffer solution with a desired pM-value can be made. If, for example, a pM-value of 6 is desired for a calibration purpose, a buffer region is established when choosing a complexing agent with $\log K_{ML} = 14$ and $\log K_{NL} = 9$, and preparing a solution with $C(N) = C(M)$.

The two equivalence points, (pM_{eq1}) and (pM_{eq2}), are important since they set limits to the three buffer regions in Fig. 2. The first buffer region is between $pC(M)$ and (pM_{eq1}), the second between (pM_{eq1}) and (pM_{eq2}), and the third when $pM > (pM_{eq2})$. The pM-values for the two equivalence points will be calculated below. They can also be estimated with logarithmic diagrams (ref. 3).

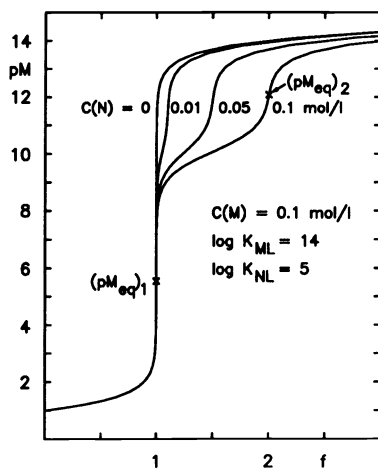


Fig. 2. Titration curve when a solution containing two metal ions, M and N, is titrated with a chelating agent, L.

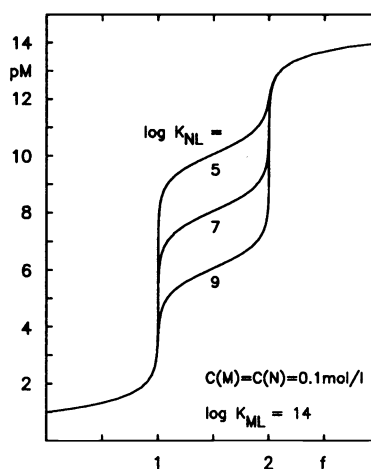


Fig. 3. Titration curve when a solution containing equimolar concentrations of the two metal ions, M and N, is titrated with a chelating agent, L. The effects of changing the value of $\log K_{NL}$ are shown.

At the first equivalence point the reaction $M + L = ML$ has proceeded as far to the right as possible, that is, $[M]$ will be as small as possible, and the reaction $N + L = NL$ will have progressed to the least possible extent, that is, $[NL]$ will be as low as possible.

Therefore, the equivalence point will be found at a pM -value where $[M] = [NL]$, that is, when

$$[ML]/([L] K_{ML}) = [N][L] K_{NL} \quad (24)$$

At the first equivalence point $[ML] = C(M) - [M]$. If $\log K_{ML} > 8$ the approximation $[ML] \cong C(M)$ is justified. At the same point $[N] = C(N) - [NL] \cong C(N)$. Equation (24) can now be written

$$pL = (\log K_{ML} + \log K_{NL} - (pC(N) - pC(M)))/2 \quad (25)$$

Using equation (3) the $(pM_{eq})_1$ -value can be calculated from

$$(pM_{eq})_1 = (\log K_{ML} - \log K_{NL} + pC(M) + pC(N))/2 \quad (26)$$

The numerical value of $(pM_{eq})_1$ in Fig. 2 is thus $= (14 - 5 + 1 + 1)/2 = 5.5$.

The same equation can be derived from equation (11) assuming that both α_{ML} and α_M are unity and that α_L is only dependent on the side-reaction between L and N, that is (ref. 1)

$$\alpha_L = ([L] + [NL])/[L] = 1 + [N] K_{NL} \quad (27)$$

If the metal ion N is present in sufficient excess over L (which is the case at the first equivalence point) and if N does not react with other solution components, that is, if $C(N) = [N]$, equation (27) can be written

$$\alpha_{L(N)} = 1 + C(N) K_{NL} \cong C(N) K_{NL} \quad (28)$$

The conditional constant for ML is then, since $\alpha_L = \alpha_{L(N)}$

$$K_{ML}^{M,L'} = K_{ML}/\alpha_{L(N)} = K_{ML}/(C(N) K_{NL}) \quad (29)$$

Taking logarithms and denoting that $(\log K_{ML} - \log K_{NL}) = \Delta \log K$, equation (29) can be written

$$\log K_{ML}^{M,L'} = \Delta \log K + pC(N) \quad (30)$$

At the first equivalence point, where $[M] = [L']$ and $[ML] = C(M)$, the following equation is valid

$$[M]_{eq} = ([ML]/K_{ML}^{M,L'})^{1/2} \cong (C(M) C(N) K_{NL}/K_{ML})^{1/2} \quad (31)$$

When this equation is presented in logarithmic form, equation (26) is obtained.

At the second equivalence point $[N] = [L]$ and $[NL] = C(N) - [N] \cong C(N)$ if $\log K > 4$. (ref. 1)

From the expression for K_{NL} the following equation can be derived

$$pL = (\log K_{NL} + pC(N))/2 \quad (32)$$

Inserting this value in equation (3) and noting that $[ML] \cong C(M)$ one gets

$$(pM_{eq})_2 = pC(M) + \log K_{ML} - (pC(N) + \log K_{NL})/2 \quad (33)$$

The numerical value of $(pM_{eq})_2$ in Fig. 2 is thus $= 1 + 14 - (1 + 5)/2 = 12$.

In the buffer region between the two equivalence points (pM_{eq1} and pM_{eq2}) the pM -values can be calculated approximately by means of the following equation, which is obtained when equations (3) and (21) are combined

$$pM = \log(K_{ML}/K_{NL}) + pC(M) + \log([NL]/[N]) \tag{34}$$

If $K_{ML} > K_{NL} > 10^7$ the two concentrations in the last term can be expressed by

$$[NL] = C(L) - C(M) \quad \text{and} \quad [N] = C(M) + C(N) - C(L)$$

From equation (34) it is evident that the pM -value is affected if the solution is diluted. The best buffer region is found close to the point where $C(L) = C(N)/2 + C(M)$.

Note: If $\alpha_{L(N)}$ and $\alpha_{L(H)}$ are of the same order of magnitude, an over-all side-reaction coefficient (ref. 1) must be taken into account in the calculations.

The over-all coefficient can be calculated using the following equation

$$\alpha_L = \alpha_{L(N)} + \alpha_{L(H)} - 1 \tag{35}$$

Referring to equation (12) a general expression for the over-all coefficient is

$$\alpha_X = \alpha_{X(Y_1)} + \alpha_{X(Y_2)} + \dots + (1 - s) \tag{36}$$

where s is the number of different interfering species in the solution.

3. TWO-PHASE SYSTEMS

3.1 Metal buffering using a liquid-liquid extraction system

There are two different ways to prepare a metal buffer in a system consisting of two liquid phases, one phase being aqueous:

- A. When both the metal complex and the complex-forming ligand partition between the organic and the aqueous phase.
- B. When only the complex-forming ligand partitions between the organic and the aqueous phase.

These two systems are shown diagrammatically in Fig. 4.

The theoretical treatment derived by Ringbom and Still (ref. 4), based on the concept of conditional extraction constants, can be used to express the pM -value in the aqueous phase.

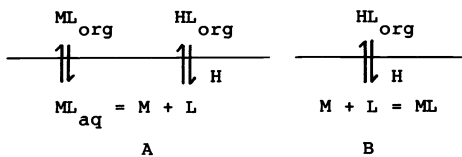


Fig.4. Partitioning of A) the metal complex and the complex forming ligand, B) the complex forming ligand between the organic and the aqueous phase.

A. Both metal complex and legend are partitioned . The main reaction is in this case



with the extraction constant

$$E_{ML} = [ML]_{org}/([M][L]) \quad (= K_D(ML) K_{ML}) \tag{38}$$

where $K_D(ML)$ is the partition coefficient for the metal complex, that is,

$$K_D(ML) = [ML]_{org}/[ML] \tag{39}$$

Using the conditional extraction constant, defined as,

$$E_{(ML)'}^{M',L'} = \alpha_{ML} E_{ML} / (\alpha_M \alpha_L) \quad (40)$$

the pM'-value of the aqueous phase can be calculated from

$$pM' = \log E_{ML} - \log \alpha_M + \log(\alpha_{ML}/\alpha_L) + \log([L']/[ML]_{org}) \quad (41)$$

or

$$pM = \log E_{ML} + \log(\alpha_{ML}/\alpha_L) + \log([L']/[ML]_{org}) \quad (42)$$

It is seen that equations (41) and (42) are analogous to equations (16) and (17) in the previous section, the only obvious difference being the way in which E_{ML} is defined. Other differences are found when the side-reaction coefficients are examined in detail.

The ligand L will in the two phase system be partly transferred to the organic phase as HL. This can be considered as a side-reaction:



with the corresponding extraction constant

$$E_{HL} = [HL]_{org}/([H][L]) (= K_D(HL) K_{HL}) \quad (44)$$

where $K_D(HL)$ is the partition coefficient of the protonated ligand and K_{HL} the proton stability constant (see equation (15)).

The side-reaction coefficient is therefore

$$\alpha_{L(org)} = ([L] + (V_{org}/V_{aq})[HL]_{org})/[L] \quad (45)$$

or

$$\alpha_{L(org)} = 1 + (V_{org}/V_{aq})[H] E_{HL} \quad (46)$$

where V_{org} and V_{aq} are the volumes of the two phases. The ligand is thus considered as being in the aqueous phase and the fact that it is partly in the organic phase is taken into account by the coefficient $\alpha_{L(org)}$.

The formation of ML in the aqueous phase is in this case considered as a side-reaction to M (L being present in excess), with the corresponding side-reaction coefficient $\alpha_{M(L)}$, defined by

$$\alpha_{M(L)} = 1 + [L] K_{ML} = 1 + [L'] K_{ML}/\alpha_L \quad (47)$$

In all other respects, the same treatment as already given in the previous section applies in the two phase system. The organic phase will act as a reservoir for the metal complex and the ligand. The buffer capacity may therefore be increased substantially by use of a two phase buffer system in cases when the ligand or the metal complex are only sparingly soluble in the aqueous phase.

The range of maximum buffer capacity is shifted from the value obtained in a single phase system. In the case of two phase pH buffer systems, theory for the shift in buffer capacity has been derived by Janjić and Milosavljević (ref. 5). Janjić *et al.* have also discussed multicomponent two phase buffer systems (ref. 6), two phase buffer systems in which acid dimerization occurs in the organic phase (ref. 7), and two phase buffer systems with diprotic acids (ref. 8). Similar theories for two phase metal buffers have yet to be derived.

Since the side-reaction coefficient $\alpha_{L(org)}$ will depend on the phase volume ratio, the pM-value will also depend on this ratio. This is of course a disadvantage of the two phase systems.

B. Only complex-forming ligand is partitioned. The theory outlined in Section 2 above applies, the partitioning of the ligand between organic and aqueous phase being considered by aid of the side-reaction coefficient $\alpha_{L(\text{org})}$ (see equation (46)). In this partition, the phase volume ratio will also influence the pM-value of the buffer.

The following example illustrates the use of an extractive system for the preparation of a metal buffer.

Example 4. To 100 mL of an 0.0005 M silver nitrate solution (pH = 5) was added 100 mL of an 0.001 M dithizone solution in chloroform, and the mixture thoroughly shaken. The silver complex does not participate in side-reactions in the organic phase. Calculate the pAg-value a) in the aqueous solution, b) in the aqueous solution if it were diluted to double its volume before adding the reagent solution. The constants are (ref. 1) $\log E_{\text{AgL}} = 15.7$, $\log E_{\text{HL}} = 10.2$.

$$\text{a) } [\text{AgL}]_{\text{org}} = 0.0005 \text{ M and } [\text{L}'] = 0.0005 \text{ M,} \quad \alpha_{L(\text{org})} = 1 + 10^{-5} 10^{10.2} = 10^{5.2},$$

Using equation (42), $\text{pAg} = 15.7 - 5.2 = 10.5$.

$$\text{b) } [\text{AgL}]_{\text{org}} = 0.0005 \text{ M and } [\text{L}'] = 0.00025 \text{ M,} \quad \alpha_{L(\text{org})} = 1 + (10^{-5} 10^{10.2})/2 = 10^{4.9},$$

and thus $\text{pAg} = 15.7 - 4.9 + \log(0.00025/0.0005) = 10.5$.

The results of the calculation in Example 4 shows that dilution of the aqueous solution does not change the pAg-value. If the pH-value of the aqueous solution is changed by one logarithmic unit, the corresponding pAg-value also change by one logarithmic unit.

3.2. Metal buffering using a chelating ion-exchanger system

Hendrickson, Turner and Corey (ref. 9) have recently described a new approach to preparation of metal buffers. This uses a two-phase system consisting of an aqueous solution and a chelating ion exchange resin. In such a system several ion exchange equilibria may be operative.

In the simplest case, the solution will contain only hydrogen ions (H^+) and a metal ion (M^{z+}). The resin is prepared by loading the protonated form partly with metal ions. When the resin is added to the solution, an equilibrium will be formed between the two phases, such that



where R^- represents the resin matrix and H^+ is the counter ion. The equilibrium may be described by the selectivity coefficient

$$K_{z\text{H}}^{\text{M}} = [\text{M}]_{\text{r}} [\text{H}]^z / ([\text{M}] [\text{H}]_{\text{r}}^z) \quad (49)$$

where concentrations in the resin phase are denoted by a subscript r. After rearrangement, equation (49) can be expressed in logarithmic terms as follows:

$$\text{pM} = z \text{pH} + \log K_{z\text{H}}^{\text{M}} - \log([\text{M}]_{\text{r}} / [\text{H}]_{\text{r}}^z) \quad (50)$$

As equation (50) shows, the pM-value of the aqueous solution is determined by the pH-value (that is, the concentration of counter ions) in the aqueous phase, by the selectivity coefficient and by the relative loading of M^{z+} and H^+ on the resin. Provided that the loading is high enough for the last term in equation (50) to remain practically constant as a small amount of M^{z+} is displaced from the resin into solution, the pM-value of the solution will only vary with the pH-value of the solution phase. This can be controlled by a suitable pH buffer.

Thus, at constant pH-value the pM-value of the solution will also remain constant.

The following comments apply in this case:

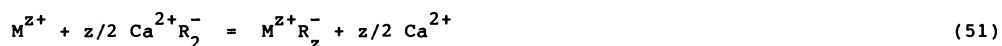
1. The M^{z+} -ions released from the resin are subject to side-reactions, e.g., hydrolysis, in the same way as for the usual metal buffers. Consequently, considerably more of M^{z+} than given by equation (48) may be displaced from the resin which may cause the last term in equation (50) to change.

2. The pM-value will not change upon dilution provided that the pH-value of the solution phase does not change.
3. A small change in pH-value will affect the pM-value to a higher degree if the metal ion is highly charged than if the charge is low.
4. Other heavy metal ions present as impurities in the solution phase will be adsorbed by the resin phase (according to their selectivity coefficients). This may be an advantage, e.g., in the calibration of ion selective electrodes of poor selectivity.
5. The side-reactions (for example hydrolysis) must be well known in order to make possible the calculation of the metal ion activity of the buffer, which is conveniently done by an appropriate alpha coefficient.

When several different metal ions are present in the solution, as, for example, in natural waters, the equilibria become more complicated, but an ion exchange resin may also be used to maintain a constant activity of one of the metal ions. In many natural waters, calcium ion is the principal species which acts as a counter ion for the ion exchange of heavy metals. The calcium ion will therefore be used in the following example to describe the working principles of the metal buffer chelating resin.

The resin is prepared by loading it with calcium and M^{z+} ions at a defined pH-value, which will yield a resin partly loaded with M^{z+} ions, partly with calcium ions and partly with hydrogen ions.

In this case the simple equilibrium (48) will be replaced by several equilibria:



Two reactions (equations (51) and (52)) will affect the pM-value of the solution phase and it will be necessary to control both the pH- and the pCa-value of the solution in order to get the desired pM-value. This type of buffer resin has its main application in speciation of natural waters (ref. 9).

It may, however, be mentioned that it is often possible to use ion selective electrodes to measure the pH- and the pCa-value of the solution and then calculate the pM-value by semi-empirical equations such as those given by Hendrickson, Turner and Corey (ref. 9). This may prove useful when the activity of M cannot be measured directly as is often the case at low activity levels.

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