The Liquid Junction Potential in Potentiometric Titrations. 6B. The Calculation of Potentials Across Liquid Junctions of the Type $AY|AY+BY_{z(B)}+HY+A_yL$ for Cells where Weak Complexes are Formed at $[A^+]=C$ M Constant and $-\log[H^+]\leqslant 7$

Erzsébet Néher-Neumann

Department of Chemistry, Inorganic Chemistry, Royal Institute of Technology (KHT), S-100 44 Stockholm, Sweden

Néher-Neumann, E., 1999. The Liquid Junction Potential in Potentiometric Titrations. 6B. The Calculation of Potentials Across Liquid Junctions of the Type $AY|AY+BY_{z(B)}+HY+A_yL$ for Cells where Weak Complexes are Formed at $[A^+]=C$ M Constant and $-\log[H^+]\leqslant 7$. – Acta Chem. Scand. 53: 997–1002. © Acta Chemica Scandinavica 1999.

Equations are derived for the calculation of the total cell EMF of cells where formation of weak complexes takes place at $[A^+]=C$ M constant and at a high concentration of $[B^{z(B)+}]=B_T$ constant (self-medium method). T denotes total. This can be defined at 25 °C as

$$E_J = E_{0J} + (59.16/z_J) \log c_J f_{JTS2} + E_D + E_{Df}$$

Here, c_J is the concentration and z_J is the charge of the potential determining ion J, TS2 denotes the terminal solution $2 \equiv$ test solution, f_J is the activity coefficient of ion J around the measuring electrode, E_D is the ideal diffusion potential, E_{Df} is the contribution of the activity factors to E_D. The cells have liquid junctions of constant ionic medium type: $AY|AY+HY+BY_{z(B)}+A_yL$. They are assumed to contain equilibrium solutions which exist in the system $HY-BY_{z(B)}-A_yL$ in the ionic medium (A^+,Y^-). Here, L^{y-} denotes the ligand. E_{0J} is an experimental constant. The cells have indicator electrodes reversible for the $B^{z(B)+}$ (cell B) and H^+ ions (cell H), respectively. $B^{z(B)+}$ is the central metal ion. Some of the equations obtained were tested in a study of the formation of the hydrogencarbonate and carbonate complexes of the lead(II) ions.

This work is Part 6B of the series and deals with the calculation of the total cell EMF E_B and E_H, which includes the total potential anomalies (ΔE_B and ΔE_H) and where weak complexes are formed. The test solution is supposed to be identical with the equilibrium system which appears between the reacting species $BY_{z(B)}-HY-A_yL$ in the ionic medium (A^+,Y^-) at the experimental condition $[A^+]=C$ M kept constant and $[B^{z(B)+}]=B_T$ has a high and constant value. The method of investigation is that of potentiometric titrations. The earlier parts are presented in Refs. 1–6.

In the study of weak complex formation, the measured EMF changes are small and the composition of the ionic medium is greatly changed in the self-medium method. Therefore, relatively small systematic errors can have a significant influence on the interpretation of the potentiometric titration data. Therefore, it is necessary to investigate the magnitude of the eventual systematic errors.

Symbols generally used throughout this series are presented in Part 1.[1] Symbols and definitions valid in equilibrium systems are given in Part 5.[5] The general deduction of the potential functions for the total potential anomalies in cells containing mixtures of strong electrolytes and the conditions of the deductions are discussed in Part 1.[1] Cells with the formation of strong complexes are treated in Parts 5 (Ref. 5) and 6A.[6] The validity of the potential functions is discussed in Part 5.[5] The determination of the ionic molar conductivities in different mixtures of $Cd(ClO_4)_2 + HClO_4 + NaClO_4$ is discussed in Part 2 (Ref. 2) (for $[A^+]=C$ M, constant), Part 3 (Ref. 3) (for $[Y^-]=C$ M, constant) and Part 4 (Ref. 4) (for the ionic strength $I=C$ M, constant).

The fundamental EMF cell considered is the same as the one presented in Part 6A.[6] It is quoted again here.

− Reference half-cell	Bridge solution TS1 $(x = 0)$ C M AY $I(C) = C$ M $f_J^{tr} = 1$	Test solution TS2 $(x = 1)$ $[A^+] = C$ M, is kept constant I ionic strength	Electrodes$^+$ reversible to $B^{z(B)+}$ and H^+ ions.

Cell B and H

As seen, we shall measure the free equilibrium concentration of the $B^{z(B)+}$ and H^+ ions, b and h, respectively.

The formation of weak complexes is generally studied by the so called self-medium method.[7,8] This means that the total concentration of the central metal ion, $[B^{z(B)+}] = [BY_{z(B)}] = B_T$, is kept at a high and constant level during a given titration. The concentration of the ligand, $l = [L^{y-}]$, is generally kept at a low level. Therefore, some common concentration conditions are valid in cells where weak complexes are formed and the self-medium titration technique is used. These are:

$h = [H^+]$, generally present in trace amounts

$b = [B^{z(B)+}] \simeq [BY_{z(B)}] \equiv B_T \equiv c_B$

$\sum_j n_j \simeq 0$, the concentration of the negatively charged complexes, containing metal ions, is negligible

$\sum_i p_i \simeq 0$, the concentration of the positively charged complexes, containing metal ions, is negligible

$c_A = [A^+] = C$ M, constant

These common concentration conditions are valid in every cell to be studied here.

Moreover, there are also some special concentration conditions which are valid for the concentration of the ligand and that of the anion of the ionic medium, c_Y, which must be taken into account. These concentrations are dependent on the experimental conditions used during the potentiometric titration to be studied. These will be given for every particular titration to be studied.

Hence, owing to the common concentration conditions, a cell where weak complexes are formed is identical with the simple cell containing mixture of strong electrolytes (cf. Part 1),[1] with respect to the potential contribution to the total cell EMF made by the metal ion $B^{z(B)+}$ present in the test solution. Therefore, the best EMF cell for the study of weak complex formation is that one where the potential contribution of the central metal ion to the cell EMF is on a minimum level, when mixture of strong electrolytes have been present in the cell. This is the cell where the total ionic strength of the test solution, I, is kept constant (cf. Part 1).[1]

The importance of the present study is to show that the self-medium method is a useful tool for the study of weak complex formation, where the systematic errors are smaller than in the use of other titration techniques.

1. The total EMF of cell B with an amalgam indicator electrode

The total EMF of cell B is defined as follows, through the whole series.

$$E_B = E_{0B} + (g/z_B) \log b + (g/z_B) \log f_{BTS2} + E_D + E_{Df} \tag{1a}$$

where the total potential anomalies are

$$\Delta E_B = (g/z_B) \log f_{BTS2} + E_D + E_{Df} \tag{1b}$$

The purpose of our study is to determine the individual terms in the expression of ΔE_B, moreover, E_B, and to calculate b from the total cell EMF measured. This can be done in different ways, depending on the experimental conditions used.

1.1. *Weak complexes are formed in the cell with a ligand from a weak acid, if H_yL and AOH are used in separate burettes.* In this cell the following special concentration conditions are valid

$$c_A = C \text{ M} = AY + AOH_T \tag{1c}$$

$$c_Y = C + z_B c_B + HY_T - AOH_T \tag{2a}$$

$$\Delta c_Y = c_Y - C = z_B c_B + HY_T - AOH_T \equiv z_B c_B + R \tag{2b}$$

where

$$R = HY_T - AOH_T \tag{3}$$

T denotes total, analytical concentration.
Consequently, we have in the cell composition

$$c_Y = C + z_B c_B + R \text{ M} \tag{4}$$

$l = [L^{y-}]$ M

$\sum_k l_k = \sum_k [L_k^{z(Lk)}]$ M, with $k \geqslant 2$

$[H_yL]$ M undissociated complexing agent

1.1.1. *For the preliminary data treatment and for small values of* w/a we can assume, first, that the concentration of the species $L_k^{z(Lk)-}$, with $k \geqslant 2$, is negligible. It means that we consider only the presence of the species H^+, $B^{z(B)+}$, L^{y-}, A^+, Y^-. Owing to this condition our system is reduced to be the mixture of strong electrolytes. The calculation of ΔE_J in such a system was treated in Parts 1 (Ref. 1) and 6A.[6] This deduction results in the following function for the total cell EMF

$$E_B = E_{0B} + (g/z_B) \log c_B - gz_B[D(I) - D(C)] + Q(B,c_B)c_B$$
$$+ Q(B,l)l + Q(B,R)R + \text{corr} \tag{5}$$

where

$$Q(B,c_B) = g\tilde{\epsilon}(B,Y) - gF_0(\lambda_B - z_B\lambda_Y) - gz_B t_A \tilde{\epsilon}(A,Y)$$
$$+ gt_Y \tilde{\epsilon}(B,Y) \tag{6a}$$

$$F_0 = 1/[2.303 C(\lambda_A + \lambda_Y)] \tag{6b}$$

$$t_A = \lambda_A/(\lambda_A + \lambda_Y) \quad \text{and} \quad t_Y = \lambda_Y/(\lambda_A + \lambda_Y) \tag{6c}$$

$Q(B,l)$ is given by eqn. (23) in Part 6A.[6]

On the basis of $Q(B,\Delta c_Y)$, defined by eqns. (24)[6] and (2b), we have

$$Q(B,R) = (g/z_B)\tilde{\epsilon}(B,Y) + gF_0\lambda_Y - gt_A\tilde{\epsilon}(A,Y) \tag{7}$$

The term corr is defined by eqn. (32) in Part 1.[1] We assume, here, that it is negligible. The function $Q(B,c_B)$ is identical with the slope function $SL(B,c_B)$, defined in Part 1 (Ref. 1) [cf. eqns. (44) and (41)]. The function $Q(B,l)$ can be estimated in the same way as discussed in Part 6A.[6] The function $Q(B,R)$ can be calculated according to the definition [cf. eqn. (7)]. Considering the definition of the total cell EMF, E_B, it is obvious that

$$\Delta E_B = -gz_B[D(I) - D(C)] + Q(B,c_B)c_B + Q(B,l)l$$
$$+ Q(B,R)R + \text{corr} \tag{8}$$

If it was found in a separate titration, where B_T varies within the range $0 \leqslant B_T \leqslant B_{Tmax}$ and $HY_T = $ e.g. 50 mM, is kept constant, moreover $[A^+] = C$ M, is kept constant, while $[H_yL]_F$ is varied, that the undissociated molecules H_yL have an influence on E_B, eqn. (8) must be completed with the term $SL(B,H_yL)[H_yL]_F$. Here, B_{Tmax} denotes the maximum value of B_T which was studied in the cells with complex formation. The slope function $SL(B,H_yL)$ is the slope of the plot $E_B - (g/z_B) \log c_B + gz_B[D(I) - D(C)] - \text{corr}$ versus $[H_yL]_F$. F denotes formal concentration.

The treatment described above will result in preliminary b values and at further calculation preliminary chemical model, moreover equilibrium constants.

1.1.2. *As a second step, we can refine the preliminary constants found.* This procedure is suggested in Part 6A.[6] For this purpose, we can try to integrate a more complete function for E_D and E_{Df}, as described in Part 5.[5] The ideal diffusion potential, E_D, can be obtained by the graphical integration of eqn. (28) in Part 5.[5] Here,

$$\lambda_A dc_A^* = 0 \quad \text{and} \quad -\lambda_Y dc_Y^* = -\lambda_Y \Delta c_Y \, dx$$

should be inserted, as

$$c_A^* = C \text{ M} \quad \text{and}$$

$$c_Y^* = C + x(HY_T + z_B B_T - AOH_T) \equiv C + x\Delta c_Y \tag{9}$$

The activity coefficient contribution to E_D, denoted E_{Df}, can be obtained by the graphical integration of eqn. (34b), given in Part 5.[5]

1.2. *Weak complexes are formed in the cell with a ligand from a strong acid, using the salt A_yL as complexing*

agent. In this special cell the following special concentration conditions are valid:

$$l = [L^{y-}] = L_T \text{ M}$$

Here, L_T is the total, analytical concentration of the salt added.

$$\sum_k l_k \simeq 0 \quad \text{with } k \geqslant 2$$

$$c_A = C \text{ M} = AY + yl \tag{9b}$$

$$c_Y = C + z_B c_B + HY_T - yl \text{ M} \tag{10}$$

$$\Delta c_Y \equiv c_Y - C = z_B c_B + HY_T - yl \text{ M} \tag{11}$$

For the ionic strength we have

$$I = C + (1/2)(h + z_B^2 b + z_B c_B + HY_T - yl + ly^2) \tag{12a}$$

For $\log f_B$ in the test solution TS2 we have

$$\log f_{BTS2} = -z_B^2[D(I) - D(C)] + \tilde{\epsilon}(B,L)l + \tilde{\epsilon}(B,Y)\Delta c_Y \tag{12b}$$

The test solution contains $B^{z(B)+}$, H^+, L^{y-}, Y^- and A^+ ions and it is a mixture of strong electrolytes. Hence, we obtain for small values of w/a according to the deductions for this case, given in Parts 1 (Ref. 1) and 6A,[6] and the composition of the test solution (neglecting h)

$$E_B = E_{0B} + (g/z_B) \log b - gz_B[D(I) - D(C)] + Q(B,c_B)c_B$$
$$+ Q(B,l)l + Q(B,HY_T)HY_T + \text{corr} \tag{13}$$

here $Q(B,c_B)$ is the same function as that one presented in Secton 1.1.1, given by eqn. (6a) and $Q(B,HY_T)$ is formally identical with the function $Q(B,R)$, given by eqn. (7).

On the basis of eqns. (12b), (6),[6] (18),[6] and (11) we have

$$Q(B,l) = (g/z_B)[\tilde{\epsilon}(B,L) - y\tilde{\epsilon}(B,Y)] - gF_0[y\lambda_Y - \lambda_L]$$
$$- gt_A[\tilde{\epsilon}(A,L) - \tilde{\epsilon}(A,Y)y] \tag{14}$$

The function $Q(B,l)$ can be estimated as discussed in Part 6A (Ref. 6) and $Q(B,HY_T)$ can be calculated according to the definition [cf. eqn. (7)].

1.3. *Weak complexes are formed in the cell when A_yL is used as complexing agent with the anion L^{y-} from a weak acid.*

1.3.1. *There are several pK_a values.* In this cell, the special concentration conditions given below are valid.

$$l = [L^{y-}] \text{ M}$$

$$\sum_k l_k = \sum_k L_k^{z(Lk)-} \text{ M} \quad \text{with } k \geqslant 2$$

$[H_yL]$ M   undissociated acid

$$c_A = C \text{ M} = AY + yL_T$$

$$c_Y = C + z_B c_B + HY_T - yL_T \text{ M} \tag{15}$$

$$\Delta c_Y \equiv c_Y - C = z_B c_B + G \tag{16}$$

where

$$G = HY_T - yL_T \text{ M} \tag{17}$$

The ionic strength in the test solution is

$$I = C + (1/2)\left(h + z_B^2 c_B + z_B c_B + HY_T - yL_T + \sum_k l_k z_{Lk}^2 \right)$$

(18)

1.3.1.1. If the different pK_a values (dissociation constants) of the acid H_yL are well separated, we can assume the species H^+, L^{y-}, $B^{z(B)+}$, A^+, Y^- to be present in the test solution, for the preliminary treatment of the data. The presence of the products of the protolysis of the acid H_yL, $\Sigma_k L_k^{z(Lk)-}$, is neglected. In this case the equations presented under Section 1.1.1 are essentially valid. However, the potential contribution $Q(B,R)R$ should be replaced by $Q(B,G)G$, where the function $Q(B,G)$ is formally identical with $Q(B,R)$, given by eqn. (7).

1.3.1.2. If the presence of the species $\Sigma_k L_k^{z(Lk)-}$ cannot be neglected, the complete functions for E_D and E_{Df} must be integrated graphically, as given by eqns. (28) and (34b), respectively, in Part 5.[5]

1.3.2. *A simple complexing agent is used, as AL, in the titrations.* In this case, the following approximation can be used for the concentration of the ligand

$$l = [L^{-y}] \simeq L_T \equiv [AL] \text{ M}$$

Moreover, we have

$$c_A = C \text{ M} = AY + L_T$$

$$c_Y = C + z_B c_B + HY_T - L_T$$

The test solution in the cell is again a mixture of strong electrolytes. Therefore, the same treatment can be used as it was described for this case in Parts 1 (Ref. 1) and 6A.[6] For this special cell the total cell EMF will be

$$E_B = E_{0B} + (g/z_B) \log c_B - gz_B[D(I) - D(C)] + Q(B,c_B)c_B$$

$$+ Q(B,l)l + Q(B,HY_T)HY_T + \text{corr}$$

(19)

where

$Q(B,c_B)$ is the same function as earlier [cf. eqn. (6a)]
$Q(B,l)$ is identical with eqn. (14)
$Q(B,HY_T)$ is formally identical with $Q(B,R)$, given by eqn. (7).

The different $Q(B, ...)$ functions can be calculated as earlier.

As is seen, if weak complexes are formed and cell B has been used for the determination of the free, equilibrium concentration of the ions $B^{z(B)+}$, $b \equiv c_B$ and it can be calculated in some cases from one of the equations (5), (13) and (19), knowing E_{0B} and the functions involved. As $c_B \simeq B_T$, constant, during both the determination of the constant E_{0B} and the study of the complex formation, the potential term $Q(B,c_B)c_B$ is also constant and it can be incorporated into the value of E_{0B}. The constant E_{0B} can be determined as discussed in Part 1.[1] This means that we can use a conditional constant for E_{0H}, denoted E_{0H}^B, and we do not need to determine the potential contribution $Q(B,c_B)c_B$ separately.

2. The total EMF of cell H with a H^+-sensitive indicator electrode

The total EMF of cell H is defined as follows, through the whole series

$$E_H = E_{0H} + g \log h + g \log f_{HTS2} + E_D + E_{Df}$$

(20a)

where the total potential anomalies are

$$\Delta E_H = g \log f_{HTS2} + E_D + E_{Df}$$

(20b)

For $\log f_H$ in the test solution TS2 we have

$$\log f_{HTS2} = -[D(I) - D(C)] + \bar{\varepsilon}(H,L)l + \bar{\varepsilon}(H,Y)\Delta c_Y$$

(20c)

In the present study we shall determine the potential functions ΔE_H and E_H. The total cell EMF, E_H, will be used for the calculation of the equilibrium concentration of the H^+ ions, h. We shall look on the same experimental conditions as discussed in cell B. The composition of the test solutions is also the same as discussed there.

2.1. *Weak complexes are formed in the cell with a ligand from a weak acid, if H_yL and AOH is used in separate burettes.*

2.1.1. *For the preliminary data treatment and for small values of w/a* we obtain, by assuming only the presence of H^+, $B^{z(B)+}$, L^{y-}, A^+, Y^- ions

$$E_H \simeq E_{0H} + g \log h - g[D(I) - D(C)] + Q(H,c_B)c_B$$

$$+ Q(H,l)l + Q(H,R)R + \text{corr} + \text{SL}(H,\text{acid})[H_yL]_F$$

(21)

Here

$$Q(H,c_B) = gz_B\bar{\varepsilon}(H,Y) - gF_0(\lambda_B - z_B\lambda_Y) - gz_B t_A\bar{\varepsilon}(A,Y)$$

$$+ gt_Y\bar{\varepsilon}(B,Y)$$

(22)

as given by eqn. (46) in Part 1.[1] $Q(H,l)$ is given by eqn. (29) in Part 6A.[6]

On the basis of eqns. (30),[6] (2b) and (3) we have

$$Q(H,R) = g\bar{\varepsilon}(H,Y) + gF_0\lambda_Y - gt_A\bar{\varepsilon}(A,Y)$$

(23)

$[H_yL]_F$ is the formal concentration of the undissociated acid. The notation SL(H,acid) stands for the slope of the plot $E_H - g \log h + g[D(I) - D(C)] - \text{corr}$ versus $[H_yL]_F$, at constant [HY], e.g. 50 mM, and should be determined in a separate experiment.

2.1.2. If the presence of the species $\Sigma_k L_k^{z(Lk)-}$ is not negligible, a more complete function should be integrated, graphically, in order to get E_D and E_{Df} as already discussed in Section 1.1.2.

2.2. *Weak complexes are formed in the cell with a ligand from a strong acid, using the salt A_yL as complexing agent.* The composition of the test solution, given under Section 1.2, is valid, here, as well. We obtained for the total cell EMF, with the new composition of the test

solution

$$E_H = E_{OH} + g \log h - g[D(I) - D(C)] + Q(H,c_B)c_B$$
$$+ Q(H,l)l + Q(H,HY_T)HY_T + SL(H,acid)[H_yL]_F$$
$$+ corr \tag{24}$$

where $Q(H,c_B)$ is given by eqn. (22), and $Q(H,HY_T)$ is formally identical with the function $Q(H,R)$, given by eqn. (23).

On the basis of eqns. (20c), (6),[6] (18)[6] and (11) we have

$$Q(H,l) = g[\tilde{\epsilon}(H,L) - y\tilde{\epsilon}(H,Y)] - gF_0(y\lambda_Y - \lambda_L)$$
$$- gt_A[\tilde{\epsilon}(A,L) - y\tilde{\epsilon}(A,Y)] \tag{25}$$

2.3. Weak complexes are formed in the cell, when A_yL is used as complexing agent with the anion L^{y-} from a weak acid.

The composition of the test solution, given under Section 1.3, is also valid here.

2.3.1. There are several pK_a values.

2.3.1.1. If the different pK_a values of the acid H_yL are well separated, we can assume the species H^+, L^{y-}, $B^{z(B)+}$, A^+ and Y^- to be present in the test solution, for the preliminary treatment of the data. The presence of the products of the protolysis of H_yL, $\Sigma_k L^{z(Lk)-}$, are neglected. The equations presented under Section 2.1.1 are essentially valid. But the potential contribution $Q(H,R)R$ should be replaced by $Q(H,G)G$, where the function $Q(H,G)$ is formally identical with $Q(H,R)$, given by eqn. (23). G is defined by eqn. (17).

2.3.1.2. If the presence of the species $L^{z(Lk)-}$ cannot be neglected, the complete functions for E_D and E_{Df} must be integrated graphically, as given by eqns. (28) and (34b), respectively, in Part 5.[5]

2.3.2. A simple complexing agent is used, as AL, in the titrations.

The composition of the test solution is the same as under Section 1.3.2. For the total cell EMF we obtain

$$E_H = E_{OH} + g \log h - g[D(I) - D(C)] + Q(H,c_B)c_B$$
$$+ Q(H,l)l + Q(H,HY_T)HY_T + corr \tag{26}$$

where $Q(H,c_B)$ is given by eqn. (22), $Q(H,l)$ is given by eqn. (25) and $Q(H,HY_T)$ is formally identical with $Q(H,R)$, given by eqn. (23).

As is seen, if weak complexes are formed in the cell and cell H has been used for the determination of the free, equilibrium concentration of the H^+ ions, h can be calculated from one of eqns. (21), (24) and (26), in the knowledge of the constant E_{OH} and the functions $Q(H, ...)$ involved. The functions $Q(H, ...)$ can be estimated either through some slope functions or from the interaction coefficients involved and the ionic molar conductivities measured in the equilibrium solution in question, as it has been suggested in Part 6A.[6] The constant E_{OH} can be determined as discussed in Part 1.[1] The interaction coefficients involved in the Q functions, obtained here, can either be found in the literature,[9-12]

in Part 1,[1] or can be determined by EMF titrations, as will be suggested in Part 7.[13]

When using the equations, attention has to be taken to the polarity of the cell. For cells which have poles opposite to those ones defined here, for cells B and H, the functions E_B and E_H, presented above, have to be taken with the opposite sign.

As in studies of the formation of weak complexes the measured EMF change is small, it is advantageous to use high and constant metal ion concentration, $[B^{z(B)+}]$, in order to increase the accuracy of the measurements. This is assured by the self-medium method.[7] The use of this method in EMF studies is represented by Ref. 8. The coulometric[8,14,15] change of the $[H^+]$ in EMF titrations, when it is possible, combined with the self-medium method,[7,8] is also very useful for the study of the formation of weak complexes. In this case both $c_B = [B^{z(B)+}] \simeq B_T$ and the other components of the concentration of the anion of the ionic medium, such as R, HY_T or G, respectively, are constant. Hence, the corresponding potential contributions can be incorporated into E_{OH}.

The model 2.3.1 was tested at the study of the formation of the hydrogen carbonate and carbonate complexes of the Pb^{2+} ions[16] at the experimental condition $[ClO_4^-] = 3$ M is kept constant[17] [cf. Section 3.2.3 (Ref. 17)]. The total concentrations $B_T = 0.2, 0.3, 0.5$ and 0.7 M, kept constant, were studied for the lead(II) ions in the system $Pb^{2+}-H_2O-CO_2(g)$ and in the pH range $3.0 \leqslant -\log h \leqslant 4.3$. The conditional constant E_{OH}^B was determined in mixtures of $HClO_4 + Pb(ClO_4)_2 + NaClO_4$ by acid–base titration, in the presence of the Pb^{2+} ions at a constant level, as described in Refs. 1 and 16.

$$E_{OH}^B = E_{OH} - g[D(I) - D(C)] + gc_B d_3 \tag{27}$$

At the study of the complex formation, solution (1) with the composition: $2B_T$ M $B(ClO_4) + c_1$ M $IO_4 + (3 - 4B_T - c_1)$ M $NaClO_4$ and solution (2) with the composition: c_2 M $NaHCO_3 + 3$ M $NaClO_4$ were added to the test solution in equal volumes.

As at most 1% of B_T is bound in metal carbonate complexes, the dominating species in the test solution are Pb^{2+}, Na^+ and ClO_4^-. The equilibrium concentrations of the complexes formed are negligible, as is that of the ligand, $[HCO_3^-]$. The concentration of the ions has been:

$$b = [B^{2+}] \equiv c_B \cong B_T \text{ M}$$

$$c_{Na} = C + yL_T - HY_T - z_B c_B \text{ M} \tag{28}$$

$$\Delta c_{Na} = c_{Na} - C = yL_T - HY_T - z_B c_B \equiv G - z_B c_B \text{ M} \tag{29}$$

where

$$G = yL_T - HY_T \tag{30}$$

This cell has the same concentration conditions as cells in which weak complexes are formed when using Na_yL as complexing agent and the ligand comes from a weak

acid. For this cell, the following total cell EMF was obtained[17]

$$E_H \cong E_{OH} + g \log h - g[D(I) - D(C)] + Q(H,c_B)c_B$$
$$+ Q(H,G)G + \text{corr} \tag{31}$$

where the potential contribution of the H^+ ions is neglected. At $b = B_T$, $Q(H,c_B) \equiv d_3$.[1] Moreover,

$$Q(H,G) = -g\lambda_{Na}/[2.303I(\lambda_{Na} + \lambda_{ClO_4})] + gt_Y \tilde{\epsilon}(A,Y) \tag{32}$$

The term $Q(H,G)G$ was estimated at the last titration point using the highest total concentration studied: 0.7 M. Under this condition, the systematic error has maximum value. We obtained

$$Q(H,G) = -3.68 \text{ mV M}^{-1}G$$

$$L_T = 23.30 \times 10^{-3} \text{ M}$$

$$HY_T = 5.36 \times 10^{-3} \text{ M}$$

and

$$Q(H,G)G = 0.02 \text{ mV}$$

As is seen, this potential contribution is negligible in every titration studied. The maximum value of the term $yL_T - HY_T$ can reach 6.94×10^{-3} M in the present case, which is negligible. For the ionic strength we have

$$I \cong C + (1/2)[h + c_B z_B^2 + yL_T - HY_T - z_B c_B + ...] \tag{33}$$

I can be described practically by the same function as during the determination of E_{OH}^B. Therefore, the use of eqn. (34) is verified for the total cell EMF during the study of complex formation

$$E_H \cong E_{OH}^B + g \log h + \text{corr} \tag{34}$$

As is seen, here the use of the self-medium method

results in a simple function for the total cell EFM, because the potential contribution of the metal ions to E_H is constant and can be incorporated into the constant E_{OH}^B. Moreover, the contributions due to composite changes, when using a complexing agent and a strong acid, are negligible. However, this result, concerning the potential contribution of the ligand and the strong acid added, is not of general validity. Therefore, the magnitude of the total potential amomalies, ΔE_H, must be checked in each new system studied.

References

1. Néher-Neumann, E. *Acta Chem. Scand. 51* (1997) 1141.
2. Néher-Neumann, E. *Acta Chem. Scand. 52* (1998) 873.
3. Néher-Neumann, E. *Acta Chem. Scand. 52* (1998) 1075.
4. Néher-Neumann, E. *Acta Chem. Scand. 53* (1999) 1.
5. Néher-Neumann, E. *Acta Chem. Scand. 53* (1999) 314.
6. Néher-Neumann, E. *Acta Chem. Scand. 53* (1999) 557.
7. Hietanen, S. and Sillén, L. G. *Acta Chem. Scand. 13* (1959) 533.
8. Ciavatta, L., Ferri, D., Grenthe, I., Salvatore, F. and Spahiu, K. *Acta Chem. Scand., Ser. A35* (1981) 403.
9. Guggenheim, E. A. and Turgeon, J. C. *Trans. Faraday Soc. 51* (1955) 747.
10. Spahiu, K. *Carbonate Complex Formation in Lanthanoid and Actinoid Systems*, Dissertation, Royal Institute of Technology (KTH), Dept. of Chemistry, Inorganic Chemistry, Stockholm, 1983.
11. Biederman, G. In Lutze, W., Ed., *Scientific Bases for Radioactive Waste Management*, Elsevier, Amsterdam, 1982.
12. Ciavatta, L. *Ann. Chim. (Rome) 70* (1980) 551.
13. Néher-Neumann, E. Part 7. *To be published.*
14. Ciavatta, L. *Ark. Kemi 20* (1962) 417.
15. Biedermann, G. and Ciavatta, L. *Ark. Kemi 22* (1964) 253.
16. Néher-Neumann, E. *Acta Chem. Scand. 46* (1992) 231.
17. Néher-Neumann, E. Part 8. *To be published.*