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Additives Content in ZnO Films Prepared by Spray Pyrolysis

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Abstract

ZnO films containing additives like bismuth, manganese, copper or cobalt have been deposited by spray pyrolysis of precursors dissolved in water. The additive content in the final material has been measured and it can be different from its value in the starting solution. These differences are discussed by looking at the chemistry of the starting solution.

ZnO-Schichten mit Bi-, Mn-, Cu- oder Co-Additiven wurden durch Sprühpyrolyse von in Wasser gelösten Precursoren aufgebracht. Chemische Analysen ergaben, daß sich der Additivgehalt im Pyrolysat von dem der Ausgangslösung unterscheiden kann. Diese Abweichungen werden anhand der Chemie der Ausgangslösung diskutiert.

Des films de ZnO contenant des additifs tels que le bismuth, le manganèse, le cuivre ou le cobalt ont été déposés par projection-pyrolyse de précurseurs dissous dans l'eau. La quantité d'additif présente dans le matériau final a été mesurée et elle peut être différente de sa valeur dans la solution de départ. Ces différences sont discutées en prenant en compte la chimie de la solution de départ.

1 Introduction

Spray pyrolysis consists schematically of a heated substrate onto which low molar concentration solutions of various metallic–organic compounds are sprayed. In the vicinity of the substrate surface pyrolysis occurs where crystallized films are deposited. The mechanism which leads to good films in terms of adherence, crystallinity and thickness is a chemical vapour deposition (CVD) process.[1,2]

Doped ZnO films have been deposited by this method.[3,4] The interest in doping ZnO is the possibility of tailoring its electrical and optical properties.[3–7] Such films could be used in domains like electronics, optoelectronics or photo thermal conversion and could be potential competitors of materials such as SnO_2 and Indium-Tin Oxides (ITO). Recent experimental data have shown that the dopant quantity in the film can be different from its content in the starting solution,[8] which can be detrimental when specific quantities of additives are required in the final material. However, the causes of these differences remain unexplained. In the present paper, the authors have studied this last aspect for ZnO films containing additives (bismuth, manganese, copper or cobalt) by focussing on the chemistry of the starting solution and additive nature.

2 Experimental Procedure

The zinc oxide films containing additives were obtained by the pyrolysis of an aerosol of controlled droplet size (average diameter: 4·3 μm) produced by an ultrasonic system[9] (frequency: 920 kHz) onto a heated alumina substrate (substrate dimensions: $2{\cdot}54 \times 2{\cdot}54\,cm^2$). The substrate temperature was fixed at 425°C. The starting solution consisted of a mixture of zinc acetate, $Zn(CH_3CO_2)_2 . 2H_2O$ (Pro analysis, 99·5% min, Merck, France; initial concentration: $C_{i_{Zn}} = 0{\cdot}2$ mol/litre) and one metallic acetate, $M(CH_3CO_2)_z . xH_2O$, dissolved in water ($Cu(CH_3CO_2)_2 . H_2O$, Pro analysis, 99% min; $Mn(CH_3CO_2)_2 . 4H_2O$, Pro analysis, 98% min; $Co(CH_3CO_2)_2 . 4H_2O$, Pro analysis, 99% min, Prolabo, France; $Bi(CH_3CO_2)_3 . H_2O$, Ref. 17574,

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Alfa-Ventron Produkte, France). M represents the added element and z its charge. The chosen cations were copper, manganese, cobalt and bismuth. Their concentration (C_{i_M}) ranged from 0·004 to 0·04 mol/litre. The initial volume, V_i, was 500 cm^3. These solutions were acidified by a slight addition of acetic acid (concentration $C_A = 17{\cdot}4$ mol/litre; Rectapur, 90% min, Prolabo, France). The added volume was V_A. For solutions containing manganese, cobalt or copper precursors, the added volume V_A is 10 cm^3 and the final pH was equal to 4·2. In the specific case of bismuth additive, $V_A =$ 10 cm^3 and pH = 3·8. The atomic content of cations in the film was measured by EDS. Energy Dispersive Spectroscopy (EDS) from a surface which was the size of the micrographs (selected magnification: ×2000). The detection threshold was about 1 at.%.

3 Results

Concerning manganese, copper and cobalt, their atomic content in the film as a function of their initial percentage is plotted in Fig. 1. The relationship between these two data is linear. The ratio R(M), where

$$R(\mathrm{M}) = \frac{\text{at.\%(M) in the film}}{\text{at.\%(M) in the solution}}$$

depends on the chemical nature of the added element. It is equal to 0·25, 0·30 and 0·88 for manganese, copper and cobalt, respectively. The bismuth content in the film is at the limit of the EDS detection threshold. The microstructures are presented in Fig. 2 for pure ZnO films and for ZnO films made from solutions containing 0·02 mol/litre of each additive (bismuth, manganese, copper or cobalt). The film morphology depends on the nature of the added element and remains unchanged for the different C_{i_M} tested.

4 Discussion

In an aqueous solution possibly acidified with acetic acid, Zn^{2+}, Cu^{2+}, Mn^{2+}, Co^{2+} and Bi^{3+} can form different complexes denoted $M_jL_i^{zj-i}$, where M^{z+} is the metallic cation and L^- is the ligand which can be hydroxide OH^- or acetate $CH_3CO_2^-$ (denoted Ac^-). M^{z+} can also precipitate in the form of hydroxides $M(OH)_z\downarrow$. Table 1 presents the constants associated with each cation for the different ligands and the solubility product constants of hydroxide precipitates.[10,11] The notations correspond to the following equilibria:

$$jM^{z+} + iOH^- \rightleftarrows M_j(OH)_i^{zj-i}$$

$$M^{z+} + iAc^- \rightleftarrows M(Ac)_i^{z-i}$$

$$M^{z+} + zOH^- \rightleftarrows M(OH)_z\downarrow$$

$$\beta_{OH}(i,j,M^{z+}) = \frac{[M_j(OH)_i^{zj-i}]}{[M^{z+}]_j \cdot [OH^-]^i}$$

$$\beta_{Ac}(i,M^{z+}) = \frac{[M(Ac)_i^{z-i}]}{[M^{z+}] \, . \, [Ac^-]^i}$$

$$Ks(M^{z+}) = [M^{z+}] \, . \, [OH^-]^z$$

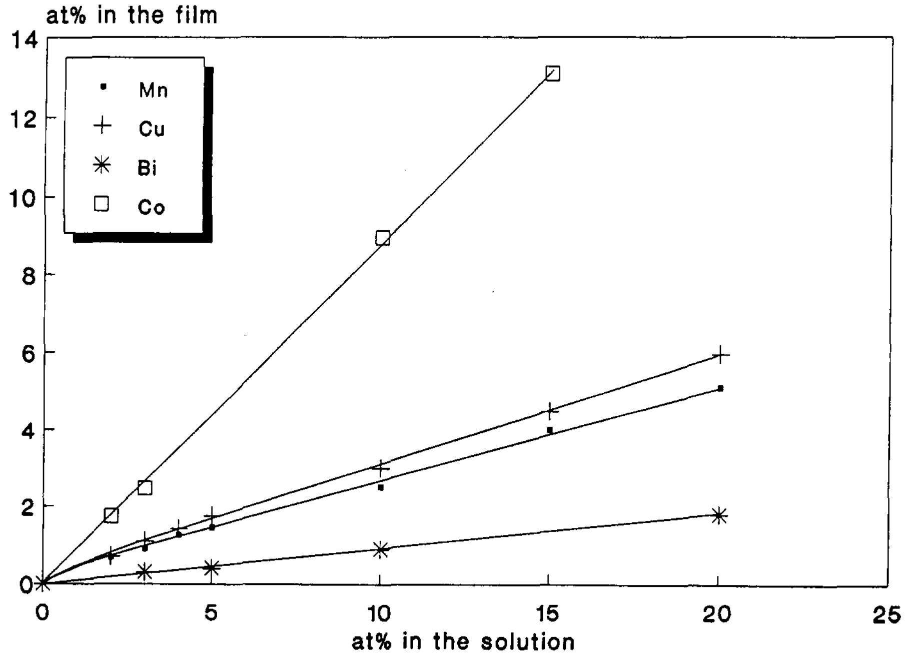

Fig. 1. Atomic content of Bi, Mn, Co and Cu in ZnO films as a function of their initial percentages.

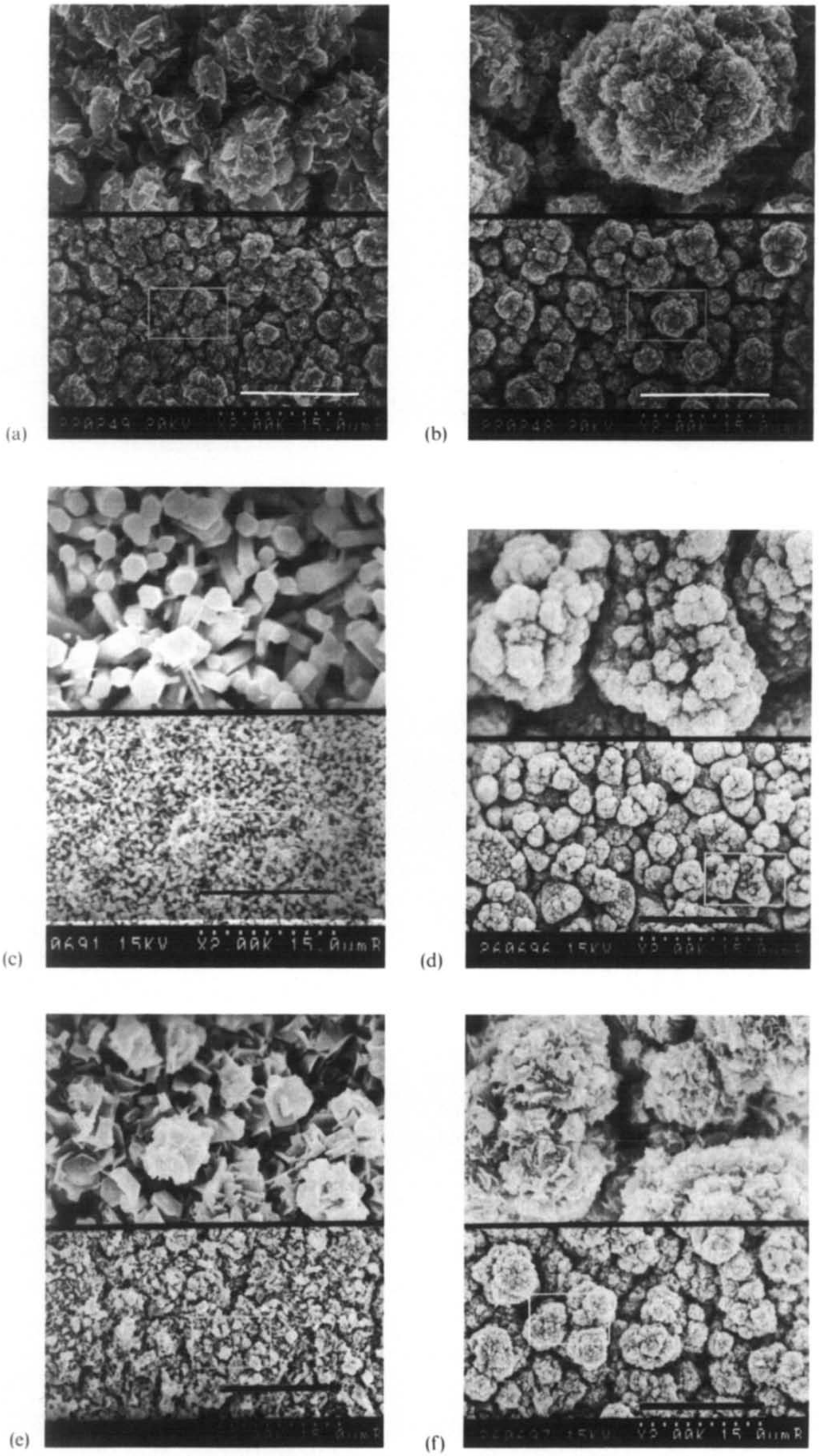

Fig. 2. Microstructures of ZnO films. Bar: 15 μm. (a) ZnO film (starting solution: pH = 3·8); (b) ZnO film (starting solution: pH = 4·2); (c) ZnO film + Bi (starting solution: pH = 3·8 and $C_{i_{\mathrm{Bi}}}$ = 0·02 mol/litre); (d) ZnO film + Mn (starting solution: pH = 4·2 and $C_{i_{\mathrm{Mn}}}$ = 0·02 mol/litre); (e) ZnO film + Cu (starting solution: pH = 4·2 and $C_{i_{\mathrm{Cu}}}$ = 0·02 mol/litre); (f) ZnO film + Co (starting solution: pH = 4·2 and $C_{i_{\mathrm{Co}}}$ = 0·02 mol/litre).

Table 1. Constants associated with hydroxide and acetate complexes and hydroxide precipitates of zinc, copper, manganese, cobalt and bismuth

Cation (M^{z+})	*log* β_{OH} (i,j,M^{z+})				*log* $\beta_{Ac}(i, M^{z+})$					*log* $Ks(M^{z+})$
Zn^{2+}	i	1	3	4	i	1	2			−16·5 to −17·4
	j	1	1	1	log β	1·3	2·1			
	log β	4·4	14·4	15·5						
Cu^{2+}	i	1	2		i	1	2	3	4	−18·8 to −19·9
	j	1	2		log β	1·7	2·7	3·1	2·9	
	log β	6·0	17·1							
Mn^{2+}	i	1			i	1	2			−12·8
	j	1			log β	0·5	1·4			
	log β	3·4								
Co^{2+}	i	1			i	1	2			−14·2 to −15·6
	j	1			log β	1·1	1·5			
	log β	5·6								
Bi^{3+}	i	1	12							−31·5
	j	1	6							
	log β	12·4	168·3							

The dissociation constant for acetic acid CH_3CO_2H (denoted HAc) can be written as:

$$\frac{[\mathrm{Ac}^-].[\mathrm{H}^+]}{[\mathrm{HAc}]} = 10^{-4\cdot75}$$

The maximum attainable pH value, pHs, without hydroxide precipitation, corresponds to the following condition:

$$[\mathrm{M}^{z+}].[\mathrm{OH}^-]^z < Ks(\mathrm{M}^{z+}) \Rightarrow \mathrm{pH} < \mathrm{pHs}$$

where

$$\mathrm{pHs} = 14 + (1/z).\log\left\{\frac{Ks(\mathrm{M}^{z+})}{[\mathrm{M}^{z+}]}\right\}$$

Table 2 presents the calculated data. For Zn^{2+} $[Zn^{2+}] = C_{i_{Zn}} = 0\cdot2$ mol/litre. An interval [pHs_1; pHs_2] is given for the added cations M^{z+} where pHs_1 and pHs_2 correspond to $C_{i_M} = 0\cdot04$ mol/litre and $C_{i_M} = 0\cdot004$ mol/litre, respectively. In the specific experimental conditions and for any cation the pH values are sufficiently low so that hydroxide precipitation has been avoided.

The remaining species are the cations and the complexes. It is possible to evaluate the critical pH value, pHc, under which the hydroxide complexes represent less than 1% of the concentration of metallic cation. The condition is written as:

$$\frac{j.[\mathrm{M}_j(\mathrm{OH})_i^{zj-i}]}{[\mathrm{M}^{z+}]} = j.[\mathrm{M}^{z+}]^{j-1}.[\mathrm{OH}^-]^i.\beta_{\mathrm{OH}}(i,j,\mathrm{M}^{z+}) < 10^{-2}$$

and pH < pHc where:

$$\mathrm{pHc} = 14 - 2/i - (1/i).\log\{j.[\mathrm{M}^{z+}]^{j-1}.\beta_{\mathrm{OH}}(i,j,\mathrm{M}^{z+})\}$$

Table 3 presents the calculated data. For $j > 1$, pHc is related to $[M^{z+}]$. Assuming that $[M^{z+}] = C_{i_M}$ an interval [pHc_1; pHc_2] is given where pHc_1 and pHc_2 correspond to $C_{i_M} = 0\cdot04$ mol/litre and $C_{i_M} = 0\cdot004$ mol/litre, respectively. The results show that at pH = 3·8, bismuth is entirely in the form

Table 2. Maximum attainable pH values without hydroxide precipitation

Cation	*pHs*
Zn^{2+}	6·1 for log Ks (Zn^{2+}) = −16·5 5·6 for log Ks (Zn^{2+}) = −17·4
Cu^{2+}	[5·3; 5·8] for log Ks (Cu^{2+}) = −18·8 [4·7; 5·2] for log Ks (Cu^{2+}) = −19·9
Mn^{2+}	[8·3; 8·8] for log Ks (Mn^{2+}) = −12·8
Co^{2+}	[7·6; 8·1] for log Ks (Co^{2+}) = −14·2 [6·9; 7·4] for log Ks (Co^{2+}) = −15·6
Bi^{3+}	[3·9; 4·3] for log Ks (Bi^{3+}) = −31·5

Table 3. Critical pHc value under which $\frac{j.[\mathrm{M}_j(\mathrm{OH})_i^{zj-i}]}{[\mathrm{M}^{z+}]} < 10^{-2}$

Complex	*pHc*
$Zn(OH)^+$	7·6
$Zn(OH)_3^-$	8·5
$Zn(OH)_4^{2-}$	9·6
$Cu(OH)^+$	6·0
$Cu_2(OH)_2^{2+}$	[5; 5·5]
$Mn(OH)^+$	8·6
$Co(OH)^+$	6·4
$Bi(OH)^{2+}$	−0·4
$Bi_6(OH)_{12}^{6+}$	[0·32; 0·74]

Table 4. Calculated concentrations of cations M^{2+} and acetate complexes MAc_i^{2-i} for different values of C_{i_M} in the case of manganese, copper and cobalt

	C_{i_M} (10^{-2} *mol/litre*)					
	0·2	*0·5*	*1*	*2*	*3*	*4*
at% of M in the solution	1	2.5	5	10	15	20
$[Mn^{2+}]$	0·13	0·33	0·66	1·37	2·11	2·89
$\Sigma[MnAc_i^{2-i}]$	0·07	0·16	0·31	0·59	0·83	1·02
$[Cu^{2+}]$	0·018	0·04	0·08	0·15	0·20	0·24
$\Sigma[CuAc_i^{2-i}]$	0·18	0·45	0·90	1·81	2·74	3·68
$[Co^{2+}]$	0·08	0·20	0·42	0·87	1·36	1·90
$\Sigma[CoAc_i^{2-i}]$	0·11	0·29	0·56	1·09	1·57	2·00

of hydroxide complexes. Since the final bismuth content in the film is hardly detectable by EDS analysis, the concentration of reactive bismuth species is very low. The hydroxide complexes have very little participation in the deposition process. Nevertheless, the microstructure of these films is significantly different from the morphologies of single ZnO (Fig. 2(a)).[12] In the present case the film is made of columns. For CVD mechanisms, the shape of the crystals is dependent upon the conditions of deposition and the values of diffusion coefficients[13] (diffusion along the substrate, diffusion restricted to the individual crystals and diffusion restricted to the individual crystal faces). The formation of columns could result from an 'infinite' surface diffusion, even along the substrate[13] and could be favoured by the presence of bismuth.

For cobalt, copper and manganese, the selected pH value (pH = 4·2) does not allow the formation of hydroxide complexes. Only the cations and acetate complexes are left in solution. Previous results on the deposition of ZnO films have shown that, among the remaining species, those which decompose in the vicinity of the heated substrate and actively participate to the film formation are acetate complexes.[12] In the present case, the concentrations of the different species can be calculated (see Appendix). The numerical values presented in Table 4 correspond to the concentrations of metallic cations and to the total concentrations of acetate complexes for each element. The calculated total concentration of acetates is lower for manganese than for copper. It could account for the smaller content of manganese in the ZnO films compared to copper. However, the data in Table 4 are probably not sufficient to explain the highest value of R(Co) despite the fact that

$$\sum_{i=1}^{2}[\mathrm{Mn(Ac)}_i^{2-i}] < \sum_{i=1}^{2}[\mathrm{Co(Ac)}_i^{2-i}] < \sum_{i=1}^{4}[\mathrm{Cu(Ac)}_i^{2-i}]$$

A possible justification for this discrepancy can be found in the substrate temperature. In fact, the substrate temperature (425°C) has been selected to ensure an important deposition rate of ZnO itself.[9] Given the data in Fig. 1, it would mean that for the added element the quantity of acetates which participate in the film growth would be in the following ascending order: manganese acetates, copper acetates and cobalt acetates. This hypothesis cannot be experimentally checked since the decomposition phenomena occurring near the substrate during a CVD process are unknown. Lastly, the morphologies of the films depend on the nature of the added element and not on its content. A complete understanding of these microstructures would require a thorough knowledge of the different diffusion coefficients mentioned by Van der Drift.[13]

5 Conclusion

The bismuth, manganese, copper or cobalt content in ZnO films prepared by spray pyrolysis depends on the chemical nature of the precursor. In order to get a measurable amount of additive in the final film, the starting solution has to fulfil certain requirements: its pH has to be sufficiently low in order to avoid hydroxide precipitation and formation of hydroxide complexes, otherwise the final material contains a little added cation, which is the case for bismuth. For zinc and added elements like manganese, copper or cobalt, acetate precursors have proved to be the appropriate species for the deposition of the material. In the final film the percentage of added element is probably dependent upon the decomposition mechanism of acetates and substrate temperature. Lastly, the morphologies of the films is governed by the chemical nature of the added element.

Appendix: Equations for the Calculation of Cations and Acetate Complexes Concentrations in the Solution Containing Zinc Acetates and one Metallic Cation: The Case of Zinc, Manganese Copper and Cobalt

In the present pH range, the total concentrations of zinc, C_{Zn}, added element M^{2+}, C_M, and acetates, C_{Ac}, can be written as:

$$C_{Zn} = [Zn^{2+}] + \sum_{i=1}^{2} [Zn(Ac)_i^{2-i}] \quad (A1)$$

$$C_M = [M^{2+}] + \sum_{i=1}^{n} [M(Ac)_i^{2-i}] \quad (A2)$$

$$C_{Ac} = [HAc] + [Ac^-] + \sum_{i=1}^{2} i.[Zn(Ac)_i^{2-i}] + \sum_{i=1}^{n} i.[M(Ac)_i^{2-i}] \quad (A3)$$

C_{Zn}, C_M and C_{Ac} are experimental data and are equal to:

$$C_{Zn} = \frac{C_{i_{Zn}}.V_i}{V_i + V_{Ac}} \quad (A4)$$

$$C_M = \frac{C_{i_M}.V_i}{V_i + V_{Ac}} \quad (A5)$$

$$C_{Ac} = \frac{2.C_{i_{Zn}}.V_i + 2.C_{i_M}.V_i + C_{Ac}V_{Ac}}{V_i + V_{Ac}} = 2C_{Zn} + 2C_M + \frac{C_{Ac}V_{Ac}}{V_i + V_{Ac}} \quad (A6)$$

The combination of eqn (A2) with the data in Table 1 gives:

$$[M^{2+}] = \frac{C_M}{1 + \sum_{i=1}^{n} [Ac^-]^i.\beta_{Ac}(i, M^{2+})} \quad (A7)$$

$$[M(Ac)_i^{2-i}] = \frac{C_M[Ac^-]^i.\beta_{Ac}(i, M^{2+})}{1 + \sum_{i=1}^{n} [Ac^-]^i.\beta_{Ac}(i, M^{2+})} \quad (A8)$$

The last unknown is $[Ac^-]$. The electroneutrality equation can be written as:

$$[H^+] + 2[Zn^{2+}] + [ZnAc^+] + 2[M^{2+}] + [M(Ac)^+] = [OH^-] + [Ac^-] + \sum_{i=3}^{n} (i-2).[M(Ac)_i^{2-i}] \quad (A9)$$

Multiplying eqns (A1) and (A2) by 2 and adding to eqn (A9) gives:

$$[H^+] + 2C_{Zn} + 2C_M = [OH^-] + [Ac^-] + \sum_{i=1}^{2} i.[Zn(Ac)_i^{2-i}] + \sum_{i=1}^{n} i.[M(Ac)_i^{2-i}] \quad (A10)$$

Substituting eqn (A3) in eqn (A10) gives

$$[H^+] + 2C_{Zn} + 2C_M = [OH^-] + C_{Ac} - [HAc] \quad (A11)$$

Lastly, introducing the dissociation constant for acetic acid in eqn (A11) gives $[Ac^-]$:

$$[Ac^-] = \frac{C_{Ac} - 2C_{Zn} - 2C_M + [OH^-] - [H^+]}{10^{4.75}.[H^+]} \quad (A12)$$

The substitution of $[Ac^-]$ in eqns (A7) to (A8) gives the calculated values of the different concentrations as a function of pH.

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