Thermodynamic modeling of aqueous electrolytic baths and corrosion in aqueous environment

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Many alloys can be produced by electrodeposition method. It requires only simple and inexpensive equipment. The preparation of new electrolytic baths is the one of main problems in development of electrodeposition method. The electrolytic bath should be homogeneous with all metals - alloy components in forms of electroactive aqueous species. The modern electrolytic baths should be also non-toxic, efficient and stable in time. The citrate electrolytes are especially attractive as the non-toxic baths for electrodeposition of metals, alloys and semiconductor materials [1-5]. Citrates form a lot of various metal complexes : different monomeric, dimeric, heternonuclear as also sparingly soluble polymeric complexes. Hence, the analysis of stability of citrate solutions and the analysis of electrodepositon of metals and alloys from citrate solutions is not simple. The thermodynamic models, which basis on the stability constants (Fig.1) are very helpful to development of the stable citrate baths as also other non-toxic complex baths (acetate, tartrate, EDTA, and more).

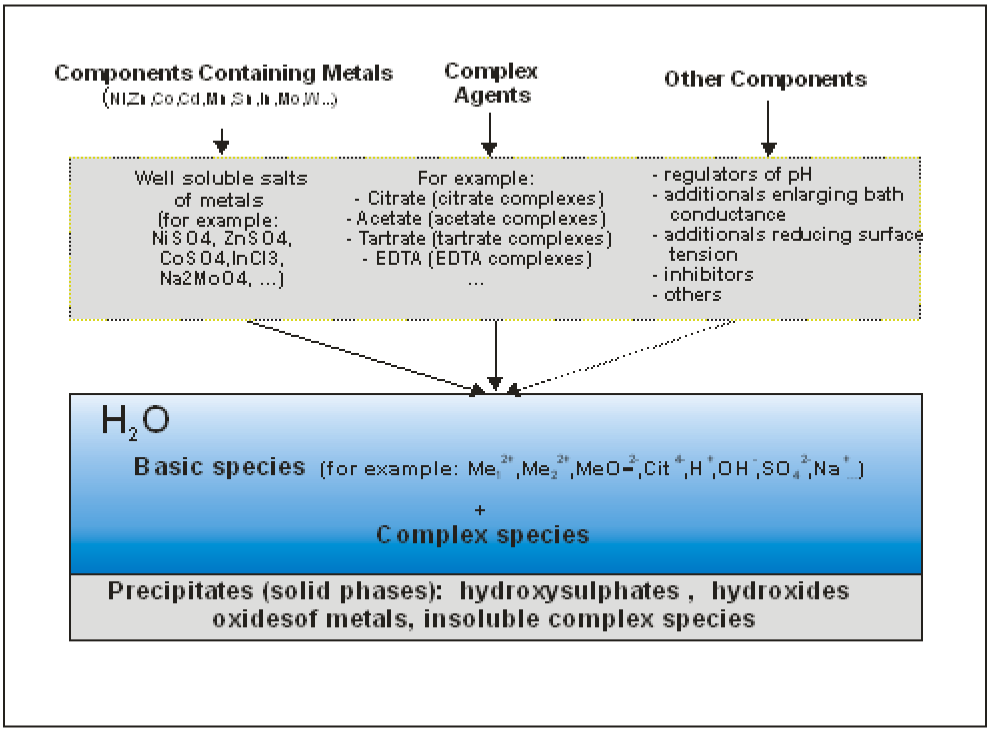

Fig. 1. Model of electrolytic bath used in themodynamic analysis [1].

The main source of stability constants data are the following databases : L.G.Sillen, A.E.Martel, „Stability Constants of Metal - Ion Complexes'' [6], NIST Critically Selected Stability Constants of Metal Complexes [7], The IUPAC Stability Constants Database (SC-Database) [8]. The only IUPAC database is still developing at present. It contains all significant stability constants and associated thermodynamic data published from 1887 with over 22000 literature references and with interactive applications to display speciation curves, to correct for temperature or ionic strength changes etc. This database contains also all stability constants included in the book volumes published by the Chemical Society, London with 1964 and 1971 [6]. Data from IUPAC database (SC-Database) may be corrected for temperature changes and for ionic strength changes using the van't Hoff equation and Davies equation respectively.

The ionic strength in real baths for electrodeposition is high. In these conditions, the methods for calculating activity constants based on the Davies equation or Debye-Hückel theory have very limited reliability hence conditional stability constants should be used in model calculation. The data from databases and the data from original literature reference can be used as the initial value for determination of conditional stability constants and for experimental verification of model as it is shown on the scheme in Fig. 2.

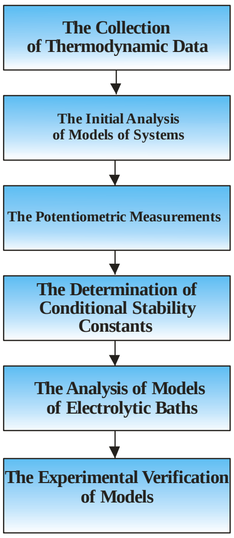

Fig. 2. The steps in creation of thermodynamic models basis on the conditional stability constants.

The potentiometric titration experiments should be performed for determination of conditional stability constants of complex species. Fig 3. shows examples of determination of conditional stability constants on the basis of titration experiments for citrate heteronuclear complexes.

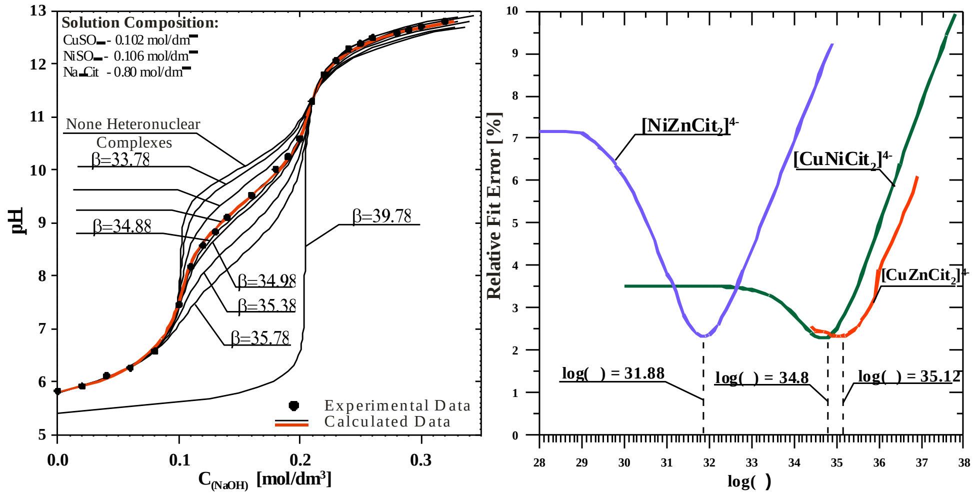

Fig. 3. The determination of conditional stability constants on the basis of titration experiments for citrate heteronuclear complexes [1].

Analysis of thermodynamic models builded on the basis of conditional stability constants allows to determine the predominant citrate complexes. This analysis allows also to indicate ranges of solution parameters within which the stable citrate electrolytes exist (i.e. sparingly soluble polymeric citrate complexes, hydrooxides and hydoroxysulphates of metals are not formed in these ranges of solution parameters). Figures 4 and 5 show examples of results of thermodynamic model analysis for baths in In(III)-Sn(II)-citrate and Sn(II)-Zn(II)-citrate systems.

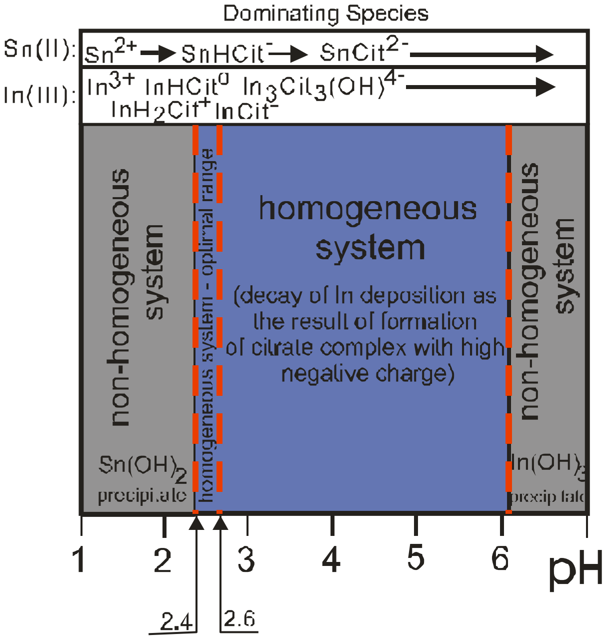

Fig. 4. The results of analysis of themodynamic model for electrolytic bath in In(III)-Sn(II)-citrate system : precipitates and predominant species. The optimal range of pH (homogenous with electroactive complexes) is very narrow : from 2.4 to 2.6.

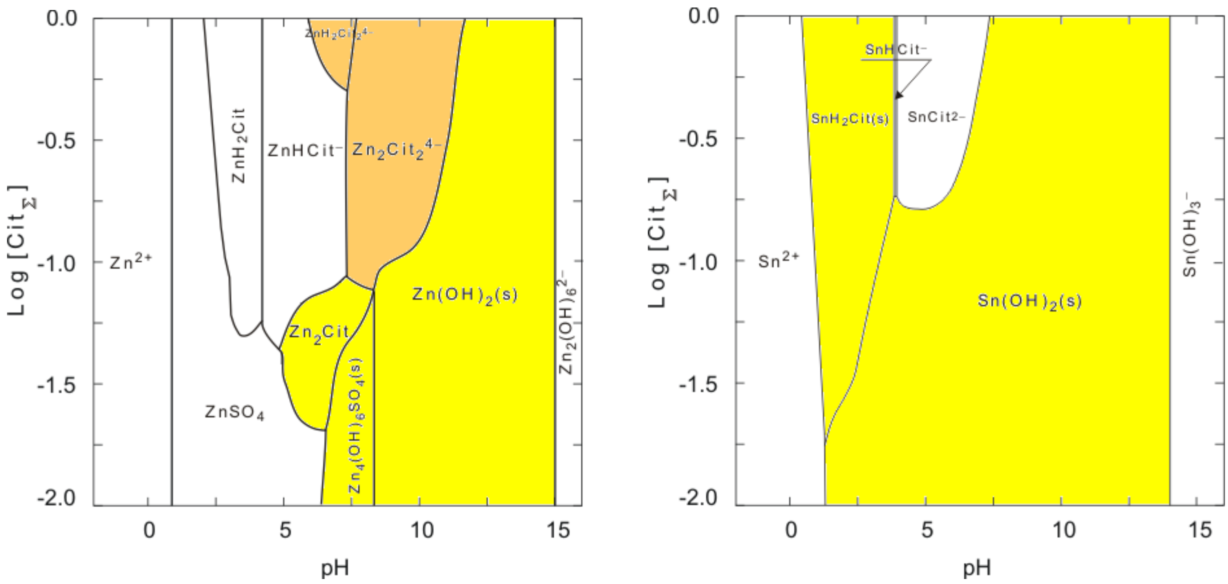

Fig. 5. The results of analysis of themodynamic model for electrolytic bath in Sn(II)-Zn(II)-citrate system - predominant species areas (precipitates - yellow areas, electroactive inactive species – brown areas and homogeneous – white areas) [2].

Analysis of thermodynamic models of solutions allows also to determine the ranges of parameters within which the little change of concentration of component is causing the great change in properties of electrolyte (e.g. pH, concentrations of the predominant species).

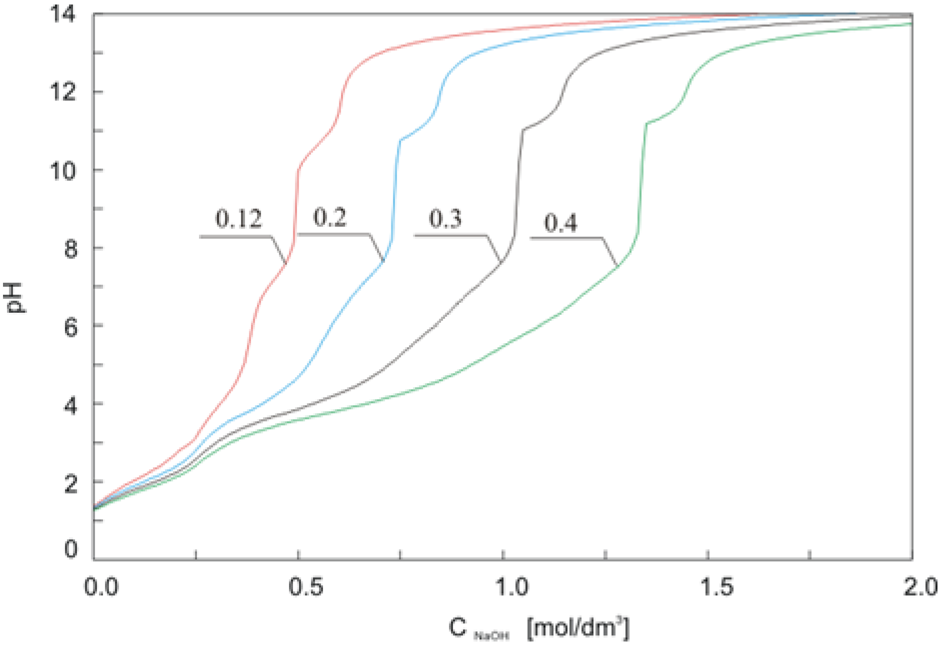

Fig. 6. The changes of pH by addition of sodium hydroxide to electrolytic bath for Zn(II)-Sn(II)-citrate system for different concentration of citrate in the bath [2].

The Fig. 6 shows the ranges of parameters within which the little change of concentration of sodium hydroxide is causing the great change in pH (jump of pH from about 8 to 10).

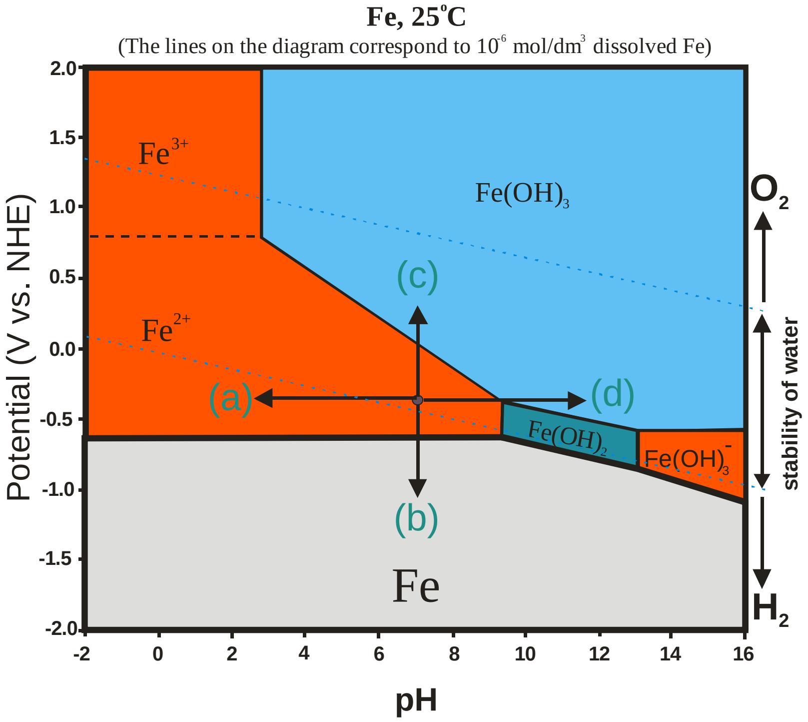

Fig. 7. The Potential-pH diagrams in the aqueous system : iron-water. Immunity/precipitates - blue areas, immunity/metal – grey area, corrosion (soluble products) – red areas. (a),(b),(c),(d) changes under (a) acidification (acidifying agent) (b) reduction (reducing agent) (c) oxidation (oxidaizing agent) (d) alkalization (alkalizing agent).

The electrodeposition proceeds with wrong reproducibility in these ranges of solution parameters if co-reduction of hydrogen(I) is present during deposition of alloys (alkalization of the near-cathodic layer of the electrolyte by process of hydrogen(I) reduction). The electrolytic bath needs the additional buffer which will be stabilized the pH in the near-cathodic layer of the electrolyte. The increase of citrate concentration in the bath decrease jump of pH in the range about 5 to 6 (Fig. 6). The citrates in this range of pH are complexing agent as well as buffer agent.

The thermodynamic models of aqueous solutions are also very useful for analysis of corrosion processes in aqueous environment. The potential–pH equilibrium diagrams for the systems element-water (Pourbaix diagrams) are collected in the “Atlas of Electrochemical Equilibria in Aqueous Solutions” by Marcel Pourbaix [9]. Fig. 7 shows the potential-pH equilibrium diagram in the aqueous system for iron-water, at 25^o. The lines on the diagram correspond to 10^{-6} mol/dm^3 dissolved iron and presence only Fe, $Fe(OH)_2$, $Fe(OH)_3$ as the solid substances is assumed (presence also other solid substances as for example iron oxides, can be also assumed). This diagram shows the influence acidification (acidifying agents), reduction (reducing agents), oxidation (oxidizing agents) and alkalization (alkalizing agents) on the corrosion and immunity of iron in iron-water system as also instability of iron in the presence of water (evolution of hydrogen). The analysis on the basis of thermodynamic models of aqueous solutions does not include kinetic effects (for example overpotential).

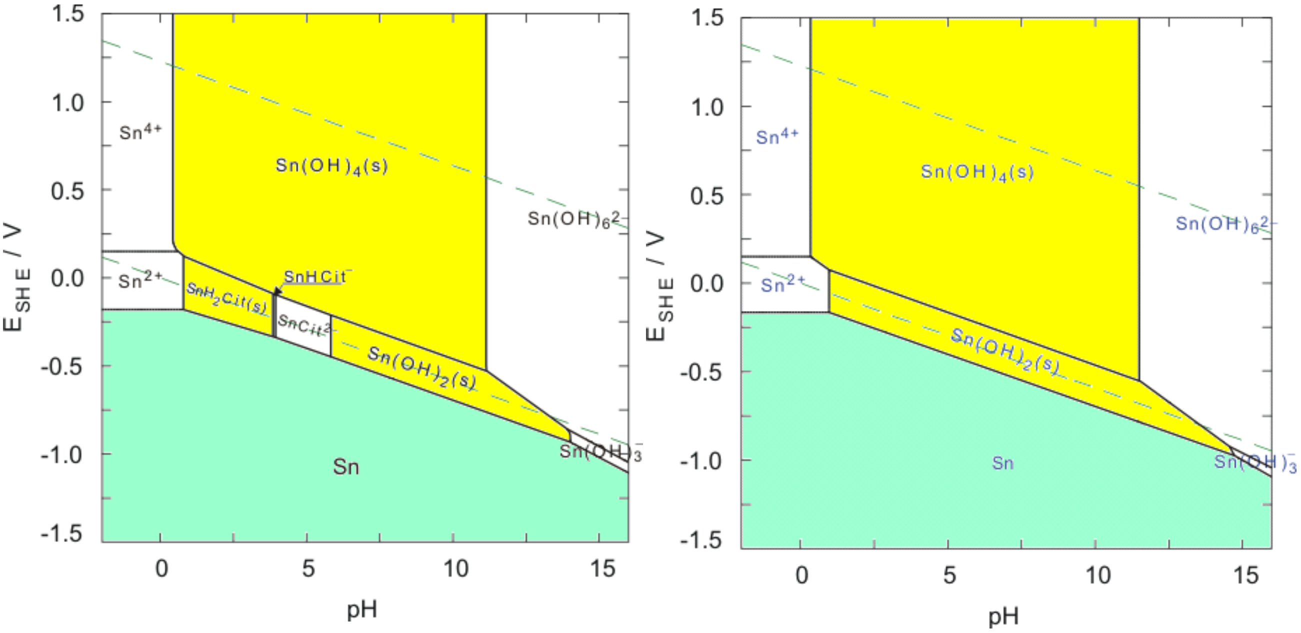

Fig. 8. The E-pH diagrams in the aqueous systems : tin-citrate-water (left, system with complexing agent) and tin-water (right). Immunity/precipitates - yellow areas, immunity/metal – green areas, corrosion (soluble products) – white areas [2].

Fig. 8 shows the potential-pH equilibrium diagrams in the aqueous systems : tin-citrate-water and tin-water. These diagrams show the influence of presence complexing agent (citrate) in solution on the corrosion and immunity of tin. The presence of complexing agent makes possible corrosion of tin in slightly acidic pH in the absence of oxidizing agents. This range of pH is also optimal for aqueous tin-citrate electrolytic baths.

Conclusions

The analysis of thermodynamic models of electrolytic bath and the results on electrochemical acitivity of complexes allow to indicate ranges of solution parameters within which:

- the stable citrate electrolytes exist;
- little change of concentration of solution component not causing the great change in properties of electrolytes;
- the electrochemical active complexes are formed.

The thermodynamic models of aqueous solutions are also very useful for analysis of corrosion processes in aqueous environment containing oxidizing, reducing, acidifying, alkalizing and complexing agents.

References :

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