



Journal of Applied Sciences

ISSN 1812-5654

science
alert

ANSI*net*
an open access publisher
<http://ansinet.com>

Mathematical Modeling of Alkali Metal Ions in Aqueous System

M.G. Mostafa

Institute of Environmental Science, University of Rajshahi, Rajshahi-6205, Bangladesh

Abstract: A simulation model was developed for Na(I)-K(I)-HCl-H₂O system to get a clear understanding of the chemical phenomena in a predictable way considering the chemical equilibria with mass and charge balance equations. The reaction between H⁺ and OH⁻ ions played a vital role in maintaining ionic equilibrium in the aqueous system. This study presents new developments and strategies to model the chemistry of alkali metal ions in aqueous system. The present model was assumed different chemical equations without having any precipitation and complex formation reactions in aqueous phase under isothermal and isobaric conditions i.e., temperature at 298K and 1 atmospheric pressure. Finally, the simulation results of the aqueous system were compared with the experimental data and very good agreement was obtained. This simulation models can be used for the development and testing of chemical phenomena in aqueous system for ionic characterization in aquifers by adapting more ions and parameters. This study showed the way of assuming the chemical phenomena of most common metal ions aqueous system.

Key words: Aqueous, model, simulation, solution, system

INTRODUCTION

Simulation of aqueous system is important in order to get better understanding of the chemical phenomena in a predictable way. Thermodynamic simulation is believed to be the most efficient way to derive aqueous phenomena without undergoing troublesome experiments. Chemical modeling has achieved tremendous development over the years and is being widely used in various branches of chemistry and chemical processes. Model assumption is a very powerful tool to predict and understand the behavior of complex aqueous systems and equally powerful in educational aspect as well.

The model simulation is being widely used in various branches of chemistry and chemical technology. An extensive literature review was done on simulation model used in chemical researches. A number of articles were found in solution chemistry including metal separation, ionic characterization, kinetic of reaction and mass transfer (Martín *et al.*, 2007; Sabaté *et al.*, 2006; Rooklidge *et al.*, 2005; Al-hamdan and Reddy, 2005). Model analysis or simulations involving chemical reactions have so far been made in many aspects. Some of them were made to determine the constants related to chemical reaction, such as equilibrium constant, solubility constant, reaction rate constant, reaction order etc. (Christov, 1998; Thomsen and Rasmussen, 1999; Berlot *et al.*, 1999).

Ions in aqueous solutions are very important in maintaining the pH and other chemical behavior. So the qualitative and quantitative analyses of them in aqueous solution play an important role in appropriate use in chemical, environmental and industrial processes. Various

ions are present in water, nonetheless, the presence of some ions beyond the tolerance limit in water would contaminate the aqueous system and become dangerous for drinking and irrigation purposes. A simple, economically feasible and ecologically sustainable model simulation process for the detection and separation of ions in aqueous system is very important to avoid troublesome experiments. Recently model simulation technique is being used in aqueous system to have a complete scenario of the chemical phenomena that can be difficult to achieve in an experiment.

This study presents a mathematical modeling for Na(I)-K(I)-HCl-H₂O system, which was developed to predict chemical phenomena of ions in the aqueous system at 25°C.

MATERIALS AND METHODS

Preparation of solutions: The solutions of NaOH and KOH were prepared separately at a concentration of 0.2 mol dm⁻³ and standardized using standard oxalic acid solution. Thus standard solutions of NaOH and KOH were set at concentrations of 0.01, 0.05 and 0.1 mol dm⁻³ separately in different volumetric flasks. Dissolving the HCl (BDH Co. Ltd.) was also made 0.2 mol dm⁻³ concentration of HCl solution and the solution was then standardized with standard NaOH solution. 0.01, 0.05 and 0.1 mol dm⁻³ concentrations of HCl solutions were made from the standardized HCl solution.

Fifty milliliter of 0.01 mol dm⁻³ HCl was titrated against 0.1 mol dm⁻³ NaOH and KOH solutions separately by continuous mixing using a magnetic stirrer. pH was

continuously measure using a pH meter. This procedure was repeated several times until more than 90 mL of total alkaline solutions were added. The whole experimental apparatuses were set inside a chamber under nitrogen gas atmosphere. The box was equipped with gas inlet and outlet to maintain the gas pressure inside the box. Nitrogen gas was supplied from out side of the box and gas flow was controlled so as to maintain 1 atm atmospheric pressure inside the box. Same procedures were repeated for the other two sets of concentrations of acid and alkaline solutions and they were 0.05 and 0.1 mol dm⁻³. A set consisted of same concentration of an acid and two alkali metals hydroxide.

RESULTS

The pH increases slowly initially with increasing metal ions concentrations, then it increases sharply and finally it reaches almost constant with increasing metal ions concentrations. These three figures show the similar tendency. The pH increases sharply near the equivalence point, from a pH of about 3 to a pH about 11. The equivalence point was attained in different metal ions concentrations at 0.01, 0.05 and 0.1 mol dm⁻³ initial concentrations of HCl solutions, respectively (Fig. 1-3).

Model

Simulation model: The significance of the present research is to assume a suitable model for an aqueous system containing common metal ions, i.e., sodium and potassium and only one anion, chloride ion for developing an adequate model to characterize sodium and potassium ions in aqueous system and reaction phenomena that take place.

Lee *et al.* (2003) has developed a chemical model of ZnSO₄-Na₂SO₄-H₂SO₄-NaOH-H₂O system to predict the hydrogen ion activity at 25°C. The study showed that the experimental pH values were in good agreement with the predicted pH values. In view of this, Na(I)-K(I)-HCl-H₂O system in the present study is described considering the chemical equilibria with mass and charge balance equations. Hydroxides of sodium and potassium and hydrochloric acid reagents are supplied to a reaction vessel containing water and they were mixed at a constant temperature and pressure. Various chemical species would be generated in the aqueous system due to chemical reactions. The model did not consider any precipitation or complex ion formation reaction and assumed only the association between H⁺ and OH⁻ ions. However, the hydration of ions is very common phenomena (Ebbing, 1996). The energy of attraction between an ion and a water molecule is due to an ion-dipole force. Water molecules are polar, so they tend to orient with respect to

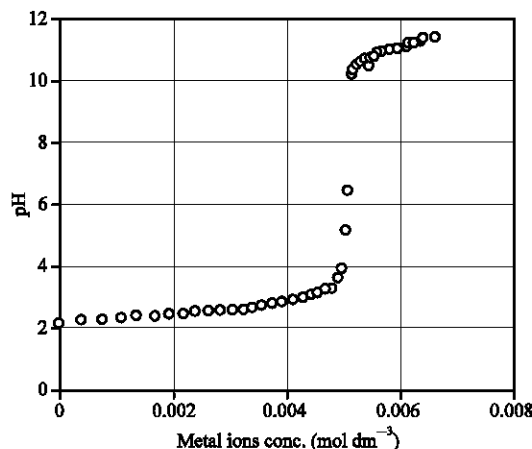


Fig. 1: Relation between metal ions concentration and pH for 0.01 mol dm⁻³ initial concentration of HCl solution at 298K

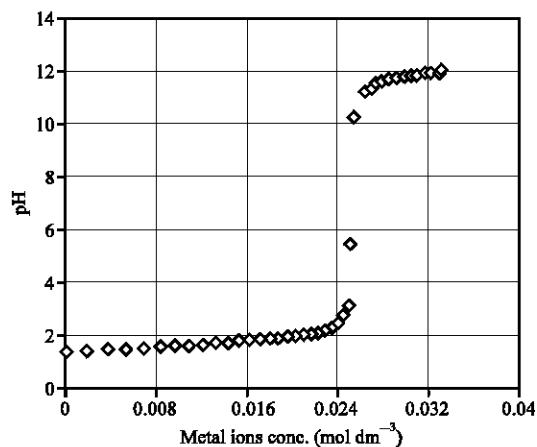


Fig. 2: Relation between metal ions concentration and pH for 0.05 mol dm⁻³ initial concentration of HCl solution at 298K

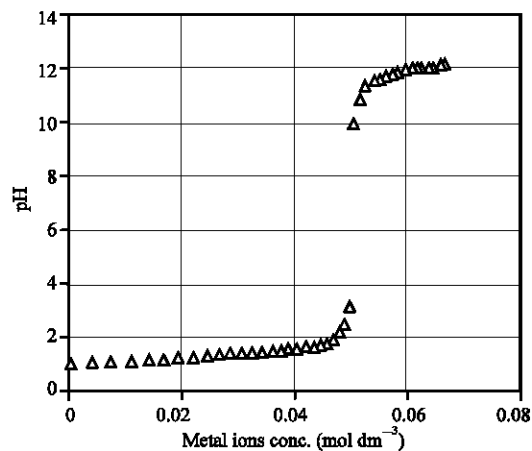


Fig. 3: Relation between metal ions concentration and pH for 0.1 mol dm⁻³ initial concentration of HCl solution at 298K

nearby ions. In the case of positive (Na⁺ and K⁺), water molecules orient with their oxygen atoms (the negative ends with the molecular dipoles) toward the ion. In the case of a negative ion (Cl⁻), water molecules orient with their hydrogen atom (the positive ends of the molecular dipoles) toward the ion. However, the hydration of ions was not considered as it has no or less significant effect on the simulation results. The charge balance equation, mass balance equation and chemical reactions in the aqueous system were taken into consideration in this model. The equilibrium reaction between H⁺ and OH⁻ ions played a vital role in maintaining ionic equilibrium in the aqueous system and that the ionic product of water was used in the model. The present model also assumed different equilibrium states among various ions in aqueous phase under isothermal and isobaric conditions i.e., temperature at 298K and 1 atmospheric pressure. A numerical programme was made based on model assumption.

Various species were assumed to be generated in the reaction vessel and their concentrations were calculated in the numerical programme using the following equations:

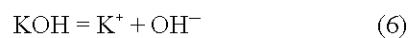
$$C(\text{HCl}) = C_i(\text{HCl}) \frac{V_i}{V_{\text{total}}} \quad (1)$$

$$C(\text{NaOH}) = C_i(\text{NaOH}) \frac{V_{\text{add}}^{\text{NaOH}}}{V_{\text{total}}} \quad (2)$$

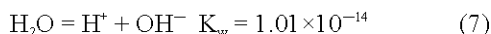
$$C(\text{KOH}) = C_i(\text{KOH}) \frac{V_{\text{add}}^{\text{KOH}}}{V_{\text{total}}} \quad (3)$$

Where, C_i(x) and C(x) are the initial concentration and concentration of a given species, x. V_i, V_{add}^x and V_{total} are the initial volume, added volume of alkaline metals hydroxide solutions and total volume of aqueous solution in the vessel.

Chemical reactions: HCl, NaOH and KOH are assumed to be completely dissociated in water and they produce the ions of H⁺, Cl⁻, Na⁺, K⁺, OH⁻. The reactions are as follows:



The ionic product of water is as follows:



Mass balance equations are

$$C_{\text{HCl}} = \text{Cl}^- \quad (8)$$

$$C_{\text{NaOH}} = \text{Na}^+ \quad (9)$$

$$C_{\text{KOH}} = \text{K}^+ \quad (10)$$

$$C_{\text{NaOH}} + C_{\text{KOH}} = \text{OH}^- \quad (11)$$

Charge balance equation

$$\text{H}^+ + \text{Na}^+ + \text{K}^+ = \text{Cl}^- + \text{OH}^- \quad (12)$$

The literature value for the ionic product of water, K_w = 1.0 × 10⁻¹⁴ (mol dm⁻³)² (Chang, 1996) was used in the model assumption. All physical and chemical conditions were considered the same in as was done in the experiment. The values thus determined, concentrations of various chemical species were computed. pH was derived by using the equation pH = -log α_H + = -log (χ_{H⁺} + [H⁺]), where χ_{H⁺} = 1 as the dilute solutions were considered in the model simulation. H⁺ ion doesn't exist in aqueous solutions as an independent species, it combines with H₂O to form H₃O⁺ and net ionic equation in acid bases reaction in water is (Sevenair and Burkett, 1996):



The existence of H⁺ or H₃O⁺ ion in aqueous system considered to be the same in this model assumption. Hence H⁺ was used in calculating pH values in the numerical program.

A numerical programme was made using Microsoft Quick Basic to compute the concentrations of different ionic species in the aqueous system.

COMPARISON OF SIMULATION RESULTS WITH EXPERIMENT

The simulation results have to compare the experimental data to check the validity of model assumption. A number of literatures were found on model simulation of aqueous system where simulation results were compared with the experimental data. A simulation model for the Co(NO₃)₂-Na₂CO₃-H₂O system based on a thermodynamic model which predicted possible equilibrium states attained among gas, aqueous and solid phases under isothermal and isobaric conditions were made by Mostafa *et al.* (2000). A theoretical and experimental result on the speciation of the Fe(II)-Fe(III)-H₂SO₄-H₂O system in concentrated solutions was studied

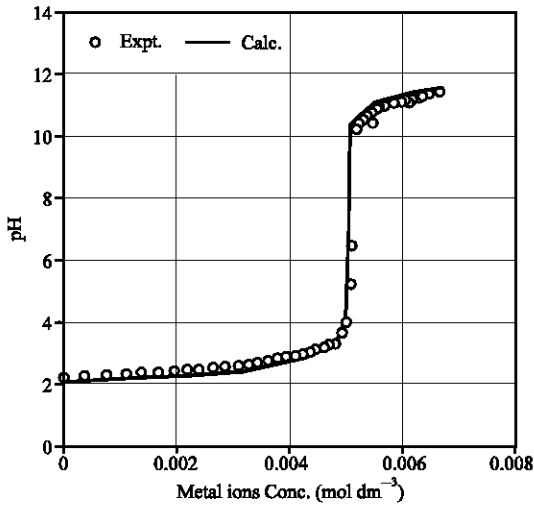


Fig. 4: Comparison of pH between simulation and experiment for 0.01 mol dm⁻³ initial concentration of HCl solution at 298K

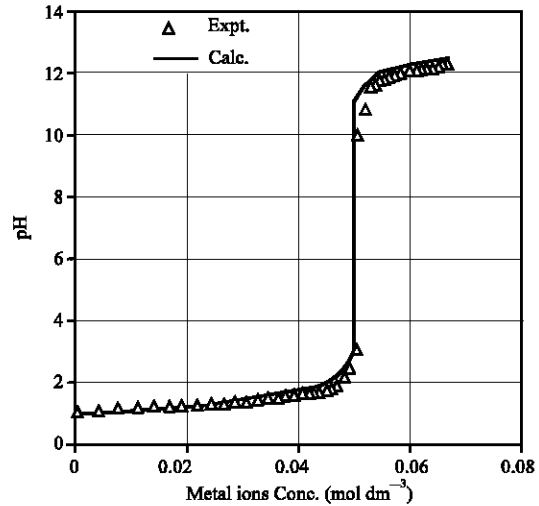


Fig. 6: Comparison of pH between simulation and experiment for 0.1 mol dm⁻³ initial concentration of HCl solution at 298K

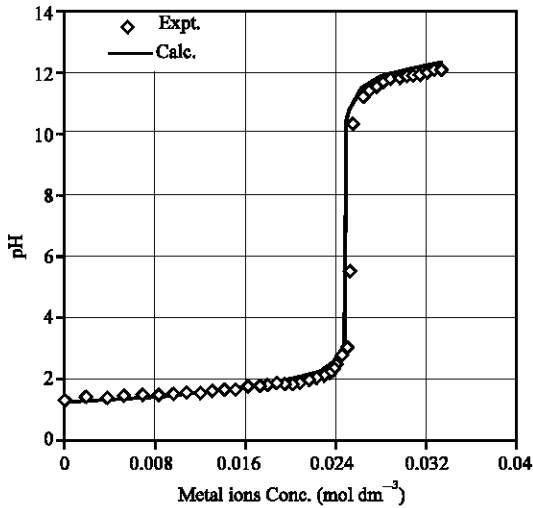


Fig. 5: Comparison of pH between simulation and experiment for 0.05 mol dm⁻³ initial concentration of HCl solution at 298K

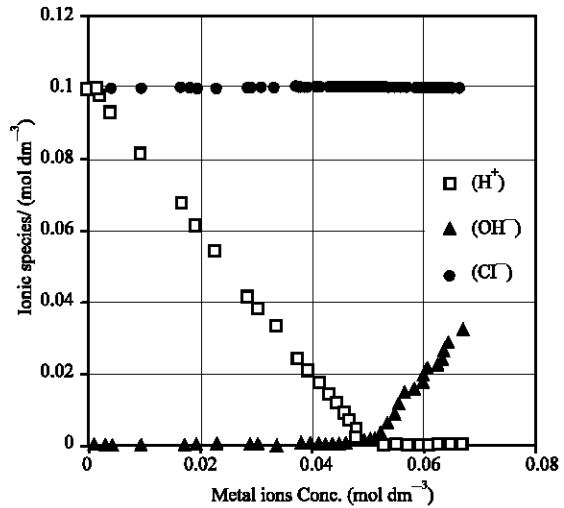


Fig. 7: Concentration of various species H⁺, OH⁻ and Cl⁻ in aqueous system with metal ions concentration for 0.1 mol dm⁻³ initial concentration of HCl solution at 298K

by Casas *et al.* (2005). Model simulations indicated that anions, cations and neutral complexes coexisted in the studied system, where the dominant species were HSO₄⁻, H⁺, Fe²⁺ and FeH(SO₄)₂. A study was carried on extraction of Zn(II) from its aqueous hydrochloric acid solutions into Alamine 336-m-xylene systems by Sayar *et al.* (2007). It was observed that the increase in acidic molarity slightly increases the extractability of Zn(II). The mathematical model simulating metal extractability in terms of organic phase Alamine volume content, aqueous phase acidic molarity and

initial metal concentration were developed. Liu and Papanagelakis (2005) presented a model the chemistry of high temperature aqueous processing systems. Monometallic sulphate solutions like Al₂(SO₄)₃-H₂SO₄, MgSO₄-H₂SO₄, NiSO₄-H₂SO₄, Fe₂O₃-H₂SO₄ were used to fit new thermodynamic parameters which were verified on progressively more complex solution mixtures. In all the above studies, simulation results were compared with available experimental data and very good agreement was found.

Both the simulation results and the experimental data show similar tendency. pH increases slowly with increasing metal ions concentrations in aqueous system initially until it reaches the equivalence point. At the equivalence point, pH increases rapidly and finally, it again increases slowly with increasing metal ion concentrations. An overall very good agreement between the simulation results and experimental data were found (Fig. 4-6). The simulation results of Fig. 7 showed the concentrations of different ionic species in aqueous system with mathematical precision that would be difficult to realize in an experiment.

A complete scenario of the chemical phenomena was thus obtained in the present model. Thus the model assumption about the chemical reactions without considering complex formation is valid.

CONCLUSIONS

Recently the model simulation of an aqueous system has widely been used to avoid complicated experimental procedure. In this study a good agreement between the simulation results and the experimental data was found. The complex formation among various cations and anions were not considered in the model and thus the comparison results justify the validity of the model assumption. However, the hydration of ions and attraction between opposite ions are very common phenomena in an ionic aqueous system and it has no significant interference in assuming the model. Moreover, the comparison results suggest that there is no metal complex ion formed in this aqueous system. The simulation results show various ions concentration in aqueous system with mathematical precision.

A well judged simulation model would provide a number of information, which would be very difficult to realize in experiments. This study could be helpful to predict the concentrations of chemical species under any stated conditions of an aqueous system. The model can be used on ionic characterization in aquifers by adapting more ions and parameters.

ACKNOWLEDGMENT

The author thanks Mr. Iqbal Bahar, Fellow in the Institute of Environmental Science, University of Rajshahi, Bangladesh for his assistance to the experiments.

REFERENCES

Al-Hamdan, A.Z. and K.R. Reddy, 2005. Surface speciation modeling of heavy metals in Kaolin: Implications for electrokinetic soil remediation processes. *Adsorption*, 11: 529-546.

- Berlot, I., P. Labbe, P. Letellier, J. Claude and D. Segal, 1999. Surface stoichiometry of ionic surfactants at interfaces: A new thermodynamic mode. *J. Phys. Chem.*, 103: 1463-1467.
- Casas, J.M., G. Crisóstomo and L. Cifuentes, 2005. Speciation of the Fe(II)-Fe(III)-H₂SO₄-H₂O system at 25 and 50°C. *Hydrometallurgy*, 80: 254-264.
- Chang, R., 1996. *Essential Chemistry*. The McGraw-Hill Companies. Inc., pp: 450.
- Christov, C., 1998. Thermodynamic study of the KCl-K₂SO₄-K₂Cr₂O₇-H₂O system at the temperature 298.15K. *CALPHAD.*, 22: 449-457.
- Ebbing, D.D., 1996. *General Chemistry*. Houghton Mifflin Company, 222 Berkeley Street, Boston, MA 02116-3764, pp: 496.
- John, P.S. and A.R. Burkett, 1996. *Acids and Bases, Introductory Chemistry-Investigating the Molecular Nature of Matter*. 1st Edn., W.M.C. Brown Publisher, pp: 543-591.
- Lee, M.S., C. K. Na, J.G. Ahn and M.H. Lee, 2003. Prediction of hydrogen ion activity in the ZnSO₄-Na₂SO₄-H₂SO₄-NaOH-H₂O system at 25°C. *Hydrometallurgy*, 68: 107-114.
- Liu, B.C.H. and V.G. Papangelakis, 2005. Chemical modeling of high temperature aqueous processes. *Hydrometallurgy*, 79: 48-61.
- Martin, A., A. Bouchard, G.W. Hofland, G.J. Witkamp and M.J. Cocero, 2007. Mathematical modeling of the mass transfer from aqueous solutions in a supercritical fluid during particle formation. *J. Supercritical Fluids*, 41: 126-113.
- Mostafa, G.M., A. Matsumoto, K. Wase and Y. Kishi, 2000. Simulation of chemical phenomena in the Co(NO₃)₂-Na₂CO₃-H₂O system based on a thermodynamic model. *Hydrometallurgy*, 57: 97-108.
- Rooklidge, S.J., E. R. Burns and J.P. Bolte, 2005. Modeling antimicrobial contaminant removal in slow sand filtration. *Water Res.*, 39: 331-339.
- Sabaté, J., M. Pujolà and J. Llorens, 2006. Simulation of a continuous metal separation process by polymer enhanced ultrafiltration. *J. Membrane Sci.*, 268: 37-47.
- Sayar, N.A., M. Filiz and A.A. Sayar, 2007. Extraction of Zn(II) from aqueous hydrochloric acid solutions into Alamine 336-m-xylene systems. Modeling considerations to predict optimum operational conditions. *Hydrometallurgy*, 86: 27-36.
- Thomsen, K. and P. Rasmussen, 1999. Model of vapor-liquid-solid equilibrium in gas-aqueous electrolyte systems. *Chem. Eng. Sci.*, 54: 1787-1802.