CCSP
Carbon Capture and Storage Program

NESTE JACOBS

Thermodynamic models for electrolyte systems

Kari I Keskinen

Porvoo, 13.5.2015

CLEEN

CONTENTS

N E S T E J A C O B S

THERMODYNAMIC MODELS FOR ELECTROLYTE SYSTEMS

1 Background

Electrolytes are met in many industrial applications where water is used as solvent. These applications are for example:

- waste water treatment

- gas scrubbing using for example amines for sulphur compound and/or carbon dioxide removal

- hydrometallurgy for production of metals

In current boom of research on the biomaterial based processes water is often present and different electrolyte systems are formed also in those systems.

As in any process design tasks, the accurate design of the equipment require good thermodynamic and transport property models in addition to the models for mass transfer and chemical kinetics.

Electrolyte systems require special thermodynamic models to take in to account the formation of ions, and precipitation/solubility of solids. Normally, most of the electrolyte systems have only water as the solvent, but mixed solvent systems are used as well. Thus, such thermodynamic models enabling mixed solvents are needed as well. For example organic compounds (acetic acid, methanol, ethanol, …) dissolved to water can form the solvent. In gas treating applications the often used thermodynamic model is the unsymmetrical choice of standard state: the gas compounds are treated as Henry components, while the solvent components dissolved in it and the ions formed are treated using a liquid phase activity coefficient model. The Henry component approach has its limitations: the dissolved gas concentration and pressure should be low.

When dealing with electrolyte systems additional information is needed: the reactions forming the ions and the parameters for the thermodynamic property calculation methods/correlations of the ions: enthalpy of formation, heat capacity at constant pressure etc.

The required amount of parameters for electrolyte systems is quite high and thus there is often no data available for certain properties and systems. Predictive methods can provide help in obtaining reasonably accurate properties and behaviour for the systems of gas, mixed solvent, electrolyte and solid.

2 The modelling target

The following phases and some examples / aspects related to them are listed below:

- Gas phase, possibly high pressure, for example in oil refining and gas treating applications

- Preferably two liquid phases, i.e. liquid-liquid equilibrium should be possible to calculate

- The liquid phases should be able to handle dissolved gases

CLEEN

NESTEJACOBS

- The liquid phases should be able to handle dissolved solids (salts or organic compounds)

- The liquid phases should be able to handle electrolytes, i.e. ions formed from dissolved gases, solids or liquid compounds

- The liquid phases should be able to handle mixed solvents, i.e. in addition to the most common solvent water, also dissolved organic compounds

- The reactions between ions in liquid phases

- Additionally, if it is possible to handle, in case of liquid-liquid systems, surface active compounds or formation of different micellar structures with solids in liquid then the applicability of the model is much widened

3 Models for electrolyte systems

3.1 Historical models

Most of the present models for electrolyte systems have been derived from the considerations of Debye and Hückel in 1923 [1].This model was the first electrolyte model which was derived from statistical thermodynamics and delivers the correct behaviour for an infinitely diluted solution of charged point particles. However, it can only be applied for highly diluted solutions.

To improve the calculation accuracy of this model at higher electrolyte concentrations, different approaches have been developed. Empirical and semi-empirical expansions have been introduced in the 1970s by Bromley [2] or [3] where especially the Pitzer model is still of major importance for the chemical industry, because a lot of parameters have been published during the last decades [4-6].

3.2 Modern models

More advanced models have been developed where the solvent can also be other than water or at least the solvent is a mixed solvent. Several gas containing applications need high pressures and then the use of Henry component approach is not very suitable, especially if the solvent includes in addition to water other solvent components (like amines). The calculation of vapour-liquid-liquid equilibrium requires liquid activity coefficient methods and then the gas compounds can in principle be handled using the Henry component approach, but a lot of parameters are needed. A better approach would be a combined approach using equation of state for gas phase and liquid activity coefficient model for liquid phase. An example of this kind of approach is the MHV2 mixing rule with SRK equation of state and suitable liquid activity coefficient model. Normally, the MHV2 is combined with the SRK equation of state and predictive UNIFAC method for the liquid activity coefficient, with special gas groups in the UNIFAC part fitted for this method. Unfortunately, these kinds of models are still under development for electrolyte systems.

The most advanced models used for electrolytes currently are

- electrolyte-NRTL model [21-27] (fitted binary interaction parameters)

- extended UNIQUAC [10-16] (fitted binary interaction parameters)

- LIQUAC (original) [32], modified LIQUAC (improved) [30] and revised LIQUAC (latest version, also called LIQUAC*) [29] (fitted binary interaction parameters)

- LIFAC (original) [31], modified LIFAC (improved) [30] and revised LIFAC (latest version, also called LIFAC*) [29] (uses predictive UNIFAC methods)

- MSA-NRTL [8-9] (fitted binary interaction parameters)

- MSE by OLI Systems [18-20] (fitted binary interaction parameters)

Under development is the electrolyte version of PSRK. PSRK is quite similar to MHV2 model. It is applicable to low and high pressures having gases and non-ideal liquid phases. It uses the SRK equation of state and the predictive UNIFAC liquid activity coefficient model with specially fitted gas groups. The current development of the electrolyte version of PSRK is the closest to the requirement set in this project. Unfortunately, the UNIFAC is just a predictive model and thus it cannot be as accurate as the models in which the parameters have been fitted against the VLE data of the application in hand. Anyway, the development of this kind of model will be followed closely, as in the future there is always need to use predictive models as measured data is not always available.

Based on going through the different models presented in the literature, their available parameter collections and few review articles [17, 28] the following models were selected for more detailed study in order to finally select models to be implemented in this project: the electrolyte-NRTL, extended UNIQUAC, revised LIQUAC (LIQUAC*) and revised LIFAC (LIFAC*). Other models are reviewed and if they seem to be worth the implementation that will be done, if time permits. Once the framework for the electrolyte models is built then addition of new models is easier and less time consuming. The excess Gibbs energy combined with equation of state models will be reviewed to see if any of them are already useful in solving large number of different cases.

4 Databases for electrolytes

The electrolyte models require a number of basic thermodynamic properties and equilibrium reaction data that are most conveniently used from databanks.

Traditionally Flowbat has been used as an in-house flowsheeting program mainly for hydrocarbon and organic compound simulation cases including reactors, distillation columns and heat exchangers etc. The energy variable calculation has been based on the scheme where each pure compound has the basis as standard enthalpy of formation as ideal gas (298.15 K, 100 kPa), standard Gibbs energy of formation as ideal gas (298.15 K, 100 kPa) and absolute entropy as ideal gas (298.15 K, 100 kPa). Additionally, the ideal gas c_p correlation is used and then liquid energy values are calculated using either enthalpy of vaporization or enthalpy deviation from ideal using an equation of state etc. These methods are not suitable for electrolyte systems as the ideal gas concept for ions does not work. Instead, new ways to calculate energy variables are needed. These require modifications to the Flowbat Access databanks and in the simulation program Flowbat itself.

NESTEJACOBS

4.1 Flowbat Access database

Flowbat pure component thermodynamic and physical property databank has been maintained in a Microsoft Access database. Now it has been modified to allow entering the data needed for electrolyte system calculations. The following has been added:

- Indication whether a compound is an ion and its charge. Additionally, indication of whether the compound is a radical or an element.

- SMILES notation for the compounds.

- Aqueous reference state (298.15 K and 100 kPa) infinite dilution values for enthalpy of formation, Gibbs energy of formation and absolute entropy for 1 molal solution.

- Liquid phase reference state (298.15 K and 100 kPa) values for enthalpy of formation, Gibbs energy of formation and absolute entropy.

- Solid phase reference state (298.15 K and 100 kPa) values for enthalpy of formation, Gibbs energy of formation and absolute entropy.

- Some other phase change energy variables (enthalpy of sublimation, enthalpy of melting etc.)

- Correlation parameters for different models of infinite dilution c_p of 1 molal aqueous solution.

- Correlation parameters for different models of liquid phase c_p.

- Correlation parameters for different models of solid phase c_p.

- Relative permittivity correlation parameters for different models of the solute compounds.

- Equilibrium reactions:

  - reaction equation stoichiometries

  - equilibrium constants as temperature correlations for p$K_{apparent}$

  - equilibrium constants as temperature correlations for pK_{true}

  - standard enthalpy of reaction (298.15 K, 100 kPa)

  - standard Gibbs energy of reaction (298.15 K, 100 kPa)

  - standard entropy of reaction (298.15 K, 100 kPa)

  - These will allow the calculation of the equilibrium reactions using the available data, expressed different ways

- All above data has reference citations in the database.

- A large number of electrolyte data has been collected to the databank.

4.2 Flowbat Access databank to Flowbat binary databank

The data in the Flowbat Access databank is written to a specially formatted text file. That file is then processed using a Fortran code to a Flowbat binary databank. Existing conversion programs have been modified to handle the new data items in the Flowbat

NESTEJACOBS

Access databank. Additionally, the equilibrium reaction databank values are converted by a new Fortran code to Flowbat binary equilibrium reaction databank. The equilibrium reaction databank can include, in addition to ion equilibrium reactions, any other type of equilibrium reactions.

4.3 Flowbat modification to use the new databanks

Flowbat simulation program has been modified to allow the use of the new databanks. The possibility to use the old format databanks has been retained to allow old simulation cases to be run without any modifications.

The new data items (parameters for the pure compounds and ions) are read in from the databank to new COMMON areas that are available for the calculation routines to be implemented. It is now possible also to read in these new values from the simulation input file in case the values are not yet available in the databank. Similarly, the equilibrium reaction parameters are read in from the equilibrium reaction databank and additionally the user can include missing data in the simulation input file.

This means that now the framework for including different electrolyte models is built in to Flowbat Access database, its conversion programs and in Flowbat simulation programs.

5 Solving phase and reaction equilibrium simultaneously

As listed in Chapter 2, the systems of interest usually contain multiple phases (gas, two liquid phases, solids/precipitates) and several simultaneously occurring equilibrium reactions. The aim is to solve the equilibrium composition of each phase. In equilibrium, temperature and pressure are same in all phases and the total Gibbs energy of the system has attained its minimum value.

The following approaches have been suggested for solving the governing equations:

1. System of equations is solved iteratively. Mass balances and electroneutrality condition can be inherently satisfied using reaction extents and distribution coefficients (between phases). Maximum allowed values for reaction extents can be hard to determine and thus negative concentrations are possible during the iteration. Handling of negative concentration can be problematic.

2. The equations can be solved also as initial value problem [7]. Initial values for components' amounts in each phase are set so that mass balances and electroneutrality condition are satisfied. Then mass transfer model is used for modelling the driving force between liquid phases and liquid and gas phase. Equilibrium reactions are modelled as forward and backward reactions. This method has been quite robust.

3. The total Gibbs energy can be directly minimized. Mass balances and electroneutrality condition are satisfied by using constraints. Non-linear constrained optimization problems need to be solved using special algorithms to ensure that global minimum has been attained.

At the moment, the approaches 1 and 2 have been implemented to Flowbat and tested for a system with two liquid phases and number of acid-base reactions.

In the future, the approach 3 will be implemented as well.

Further complications cause the formation and disappearance of phases. Before solving the system, it is not always clear whether some phases are formed or not. Thus, the formation or disappearance of phases needs to be tested during the calculations.

Kinetically controlled reactions need also to be included. As some of the reactions occurring are so slow that equilibrium reaction assumption is not valid, the reaction rates of these reactions have to be taken in to account. This kind of system can be solved by the approach 2 above. Other possibilities will be investigated later. It is important to solve such systems where some of the reactions are equilibrium reactions and some of them are kinetically controlled. These kinds of systems are also met in CO_2 capture by amine solutions as some steps in the reaction chain are slow.

6 References

1. Debye, P., Hückel, E, Physikalische Zeitscrift 9 (1923) 185-206.

2. Bromley, L.A., AIChE J. 19 (1973) 313-320.

3. Pitzer, K.S., J. Phys. Chem. 77 (1973) 268-277.

4. Pitzer, K.S., Mayorga, G., J. Phys. Chem. 77 (1973) 2300-2308.

5. Pitzer, K.S., Mayorga, G., J. Solution Chem. 3 (1974) 539-546.

6. Pitzer, K.S., Kim, J.J., J. Am. Chem. Soc. 96 (1974) 5701-5707.

7. Kuitunen, S., Phase and reaction equilibria in the modelling of hot water extraction, pulping and bleaching, Doctoral thesis, Aalto University, 2014.

8. Simonin, J.-P., Bernard, O., Papaiconomou, N., Kunz, W., Description of dilution enthalpies and heat capacities for aqueous solutions with the MSA-NRTL model with ion solvation, Fluid Phase Equilibria 264 (2007) 211-219.

9. Papaiconomou, N., Simonin, J.-P., Bernard, O., Kunz, W., MSA_NRTL model for the description of the thermodynamic properties of electrolyte solutions, Phys.Chem.Chem.Phys. 4 (2002) 4435-4443.

10. Sander, B., Fredenslund, A., Rasmussen, P., Calculation of vapour-liquid equilibria in mixed solvent/salt systems using an extended UNIQUAC equation, Chem. Eng. Sci. 41 (1986) 1171-1183.

11. Thomsen, K., Aqueous electrolytes: model parameters and process simulation, Ph.D. Thesis, Department of Chemical Engineering, Technical University of Denmark, Lyngby, Denmark, 1997.

12. Thomsen, K., Rasmussen, P., Gani, R., Simulation and optimization of fractional crystallization processes, Chem.Eng.Sci. 53 (1998) 1551-1564.

13. Thomsen, K., Rasmussen, P., Modeling of vapour-liquid-solid equilibrium in gas-aqueous electrolyte systems, Chem.Eng.Sci. 54 (1999) 1787-1802.

14. Iliuta, M.C., Thomsen, K., Rasmussen, P., Extended UNIQUAC model for correlation and prediction of vapour-liquid-solid equilibria in aqueous salt systems containing non-electrolytes. Part A., Methanol-water-salt systems, Chem.Eng.Sci. 55 (2000) 2673-2686.

15. Thomsen, K., Iliuta, M.C., Rasmussen, P., Extended UNIQUAC model for correlation and prediction of vapour-liquid-liquid-solid equilibria in aqueous salt

systems containing non-electrolytes. Part B., Alcohol (ethanol, propanols, butanols)-water-salt systems, Chem.Eng.Sci. 59 (2004) 3631-3647.

16. Thomsen, K., Modeling electrolyte solutions with the extended universal quasichemical (UNIQUAC) model, Pure Appl. Chem. 77 (2005) 531-542.

17. Lin, Y., ten Kate, A., Mooijer, M., Delgado, J., Loldrup Fosbol, P., Thomsen, K., Comparison of Activity Coefficient Models for Electrolyte Systems, AIChE Journal 56 (2010) 1334-1351.

18. Wang, P., Anderko, A., Young, R.D., A speciation-based model for mixed-solvent electrolyte systems. Fluid Phase Equilibria 203 (2002) 141-176.

19. Wang, P. Anderko, A., Springer, R.D., Young, R.D., Modelling phase equilibria and speciation in mixed-solvent electrolyte systems: II., Liquid-liquid equilibria and properties of associating electrolyte solutions. J.Mol.Liq. 125 (2006) 37-44.

20. Kosinski, J.J., Wang, P, Springer, R.D., Anderko, A., Modeling acid-base equilibria and phase behaviour in mixed-solvent electrolyte systems, Fluid Phase Equilibria 256 (2007) 34-41.

21. Chen, C.C., Evans, L.B., A local composition model for the excess Gibbs energy of aqueous electrolyte systems, AIChE Journal 32 (12986) 444-454.

22. Chen, C.C., Britt, H.I., Boston, J.F., Evans, L.B., Local composition model for excess Gibbs energy of electrolyte systems, AIChE Journal 28 (1982) 588-596.

23. Chen, C.C., Song, Y., Generalized electrolyte-NRTL model for mixed-solvent electrolyte systems, AIChE Journal 50 (2004) 1928-1941.

24. Chen, C.C., Britt, H.I., Boston, J.F., Evans, L.B., Two new activity coefficient models for the vapour-liquid equilibrium of electrolyte systems. In: Newman, S.A. (ed.), Thermodynamics of Aqueous systems with industrial applications, ACS Symposium Series 133, Washington, D.C., American Chemical Society 1980, 61-89.

25. Austgen, D.M., Rochelle, G.-T., Peng, X., Chen, C.C., Model of vapour-liquid equilibria for aqueous acid gas-alkanolamine systems using the electrolyte-NRTL equation, Ind.Eng.Chem.Res. 28 (1989) 1060-1073.

26. Chen, C.C., Representation of solid-liquid equilibrium of aqueous electrolyte systems with the electrolyte NRTL model, Fluid Phase Equilibria 27 (1986) 457-474.

27. Mock, B., Evans, L.B., Chen, C.C., Thermodynamic representation of phase equilibria of mixed-solvent electrolyte systems, AIChE Journal 32 (1986) 1655-1664.

28. Abutayeh, M., Thermodynamic analysis of electrolyte systems, Chem.Eng. March 2012, 48-54.

29. Mohs, A., Gmehling, J., A revised LIQUAC and LIFAC model (LIQUAC*/LIFAC*) for the prediction of properties of electrolyte containing solutions, Fluid Phase Equilibria 337 (2013) 311– 322.

30. Kiepe, J., Noll, O., Gmehling, J.,. Modified LIQUAC and Modified LIFAC. A Further Development of Electrolyte Models for the Reliable Prediction of Phase Equilibria with Strong Electrolytes. Industrial & Engineering Chemistry Research, 45(7) (2006) pp.2361-2373.

31. Yan, W., Topphoff, M., Rose, C., Gmehling, J., Prediction of vapor-liquid equilibria in mixed-solvent electrolyte systems using the group contribution concept. Fluid Phase Equilib. 162 (1999) 97-113.

32. Li, J.; Polka, H.-M. A gE model for single and mixed solvent electrolyte systems 1. Model and results for strong electrolytes. Fluid Phase Equilib. 94 (1994) 89-114.