Evaporation models for multicomponent mixtures

Ph.D. dissertation

Járvás Gábor

Supervisor

Dr. András Dallos

Doctoral School of Chemistry and Environmental Sciences

2012.

1. Abstract

This dissertation summarizes the author's results on simulations of the evaporation of multicomponent liquid mixtures having flat or curved liquid surface. The models are based on the quantum chemical description of non-ideality of liquid phase properties and take into account the possible transport phenomenas in the gas phase. The models apply the COSMO-RS theory for the estimation of vapour-liquid equilibrium of non-ideal solutions and the Maxwell-Stefan diffusion and convection theory for the calculation of gas phase transport characteristics of the components. The activity coefficients, the liquid and vapour phase compositions, the cumulative and components evaporation fluxes have been computed. Calculations for the quasi equilibrium evaporation of compounds from surface have been performed by COSMOtherm and COMSOL Multiphysics programs. The calculation results of both droplet evaporation and flat surface evaporation models are compared against experimentally determined values. It can be concluded that the models have reasonable ability for prediction of the evaporation of multi-component liquid systems.

Solubility parameters, such as Hansen Solubility Parameters, (HSPs) are widely accepted models for describing the interaction between molecules of multi-component mixtures and the estimation for activity coefficients of their components. New quantitative structure-property relationship (QSPR) multivariate nonlinear models based on artificial neural network (ANN) were developed for the prediction of the components of the three-dimensional Hansen solubility parameters using COSMO-RS sigma moments as molecular descriptors. The models for HSPs were built on a training/validation data set of compounds having a broad diversity of chemical characters (alkanes, alkenes, aromatics, haloalkanes, nitroalkanes, amines, amides, alcohols, ketones, ethers, esters, acids, ion-pairs: amine/acid associates, ionic liquids). HSP prediction was validated on a test set with various functional groups and polarity, among them drug-like molecules, organic salts, solvents and ion-pairs. COSMO sigma moments can be used as

T7. G. Járvás, A. Kondor, A. Dallos: Investigation of evaporation of layers and droplets of bioethanol-blended reformulated gasolines. *35th International Conference of Slovak Society of Chemical Engineering*, Tatranské Matliare, Slovakia, May 26-30, Proc. 104, ISBN 978-80-227-2903-1(2008)

T8. A. Kondor, G. Járvás, A. Dallos: Investigation of Transport of Fragrances in Air. *European COMSOL Conference 2007*, Grenoble, Oct. 23-24,(ISBN: 978-0-9766792-5-7) (2007)

T9. G. Járvás, A. Kondor, A. Dallos: A Novel Method to Modeling the Evaporation of the Multicomponent Mixtures. *European COMSOL Conference 2007*, Grenoble, Oct. 23-24 (ISBN: 978-0-9766792-5-7) (2007)

T10. G. Járvás, A. Kondor, A. Dallos: Computer Simulation of Evaporation and Transport of Multicomponent Mixtures in Air Using Comsol Multiphysics and COSMOtherm. MATH/CHEM/COMP 2007 Conference on the interfaces among mathematics, chemistry and computer sciences. Dubrovnik, Croatia, June 11-16, Book of Abstracts. P34 (2007)

T11. G. Járvás, A. Kondor, A: Dallos: Estimation of Hansen solubility parameters using QSPR model with COSMO screening charge density moments. *Conferentia Chemometrica 2007*, Budapest September 2-5, ISBN 978-963-7067-17-4, Abstract Book, P10 (2007)

T12. G. Járvás, A. Kondor, A. Dallos: Investigation of evaporation and transport of perfume ingredients in air with computer simulation using COMSOL MULTIPHYSICS and COSMOtherm. *COMSOL Users Conference*, Prague, Czech Republic, Oct. 27, Proc. 16 (2006)

3. Related publications

Publications containing the new scientific results of this thesis:

T1. G. Járvás, C. Quellet, A. Dallos, COSMO-RS based CFD model for flat surface evaporation of non-ideal liquid mixtures *International Journal of Heat and Mass Transfer* 54 (2011) 4630-4635 (IF: 1,898)

T2. G. Járvás, A. Dallos: Illatanyagok terjedésének vizsgálata levegőben, számítógépes szimuláció kísérletekkel. *XII. Nemzetközi Vegyészkonferencia*, Csíkszereda (Románia), október 3-8. Kiadvány. (2006)

T3. G. Járvás, A. Dallos: Modeling of Evaporation of Droplets of Multicomponent Liquid Mixtures using COSMO-RS. *COSMO-RS Symposium*, Maria in der Aue, Wermelskirchen, Germany, March 30-April 1 (2009)

T4. G. Járvás, C. Quellet, A. Dallos: Estimation of Hansen solubility parameters using multivariate nonlinear QSPR modeling with COSMO screening charge density moments. *Fluid Phase Equilibria* 309 (2011) 8-14 (IF: 2.253)

T5. G. Járvás, A. Dallos: Estimation of Hansen solubility parameters using multivariate nonlinear QSPR modeling with COSMO screening charge density moments. *Conferentia Chemometrica 2011*, Sümeg, Hungary, 2011. September 19-21. Book of Abstracts P18, ISBN 978-963-9970-15-1

T6. G. Járvás, A. Kondor, A. Dallos: Diffusion Evaporation Model of Multi-c omponent Mixture Droplets. *COMSOL Conference,* Budapest, Hungary, November 24, Book of Abstracts. P33 (2008)

excellent independent variables in nonlinear quantitative structure-property relationships using ANN approaches. The resulting optimal multivariate nonlinear QSPR models involve the five basic sigma-moments having defined physical meaning and possess suitable predictive ability for dispersion, polar and hydrogen bonding HSPs components.

2. Theses

2.1. Development of flat surface evaporation model

A novel method has been developed for modelling the isothermal equilibrium evaporation of real liquid mixtures having flat surface. The model based on the innovative combination of COSMO-RS theory for the estimation of activity coefficient, the Maxwell-Stefan equation and CFD simulation. The method is well applicable for calculation of cumulative evaporation fluxes as a function of the time during the quasi equilibrium evaporation of multi-component liquids [T1-T3, T6-T10 and T12].

2.2. Development of droplet evaporation model

A new method has been suggested for modelling the non-isothermal equilibrium evaporation of droplets of real multi-component liquid mixtures using creative combination of various methods. The model estimates the heat balance of droplet with a novel way, where CFD simulation is used to calculate the heat conducted into the droplet, applies COSMO-RS for the estimation of activity coefficient of components of evaporating liquid mixtures and describes the transport of evaporated molecules in the gas phase with Maxwell-Stefan diffusivity equations. The model is suitable for prediction of evaporation rate and lifetime of droplets of multi-component real mixtures during quasi equilibrium evaporation without forced convection [T3, T6-T10].

2.3. Model development for estimation of Hansen solubility parameters

New nonlinear models have been proposed for the prediction of Hansen Solubility Parameters using the sigma-moments calculated by COSMO-RS theory as independent variables in nonlinear quantitative structure-property relationships. Strong nonlinear correlations between sigma-moments and Hansen solubility parameters have been established by artificial neural networks. It can be concluded from the comparison of experimental data and simulation results that the proposed QSPR models are suitable for the prediction of solubility parameters of chemicals having a broad diversity of chemical characters such as alkanes, alkenes, aromatics, haloalkanes, nitroalkanes, amines, amides, alcohols, ketones, ethers, esters, acids, ion-pairs: amine/acid associates and ionic liquids [T4-T5 and T11].