Ph.D. Thesis

Modelling Equilibria by EOS

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I. Aims and preliminaries

Typical task for chemical engineers is designing separation of mixtures based on phase equilibria (distillation, extraction, absorption). For designing those processes the chemical engineers should be able to describe phase equilibria. However many times the data needed for calculation are not available, since measuring phase equilibrium data is time consuming and expensive. Because of it, the chemical engineers should use different estimation processes based on models.

There are two ways for modelling phase equilibrium data. The use of equation of state models avoids problems at near critical pressure, activity coefficient models are in trouble in that region.

The most requiring test and most fascinating application of EOS models is the extrapolation, that is the use of the model at conditions other than that of the data base (different temperature, pressure, composition, the latter may include calculation of mixture properties using pure component data or that of constituting subsystems). The good extrapolation ability is expected only if the model is theoretically sound. Even the most theoretically established models have empirical features. This is unavoidable as the physical reality is (and remains) too complex to describe it exactly. The realistic goal is a model which reflects the most relevant elements of the physical reality. Thus the model parameters are not simply constants of a flexible enough model but they have physical meaning. This supports their validity at conditions different from those contained in the data base used to fit them.

The other obvious limitation is the finite nature of available data base. In spite of the huge data banks and measurement projects, many data of scientific or newly arisen practical importance are missing, simply because they have not been measured. This justifies the efforts for improving models, as computation is (and remains) much less expensive than experimentation.

There are several successful ways for constructing EOS models.
The most traditional one, followed since the appearance of first cubic EOS used for liquid phase as well, applied also in flowsheeting packages, introduces binary parameters to correct Berthelot's law. These binary parameters necessarily carry all imperfection of the model. Several authors give empirical expressions for the dependence of the kij binary interaction parameter on composition, temperature, pressure, density. This approach is very useful in data reduction, more generally speaking, in interpolation, but its extrapolation power is modest. The success of modifications aimed at considering explicitly the structure of molecules suggests that molecular level considerations are more promising.

The second approach is to add a term to the widely used local composition models, resulting an EOS. The success is remarkable for polymer solutions, because the modification considers the volume effects, and it is very important there. Criticism may affect this procedure as it does not care the harmony between terms of the factorized partition function.

The third way, which is much used recently is to obtain a mixing rule by equating the GE expression of a cubic EOS with that of a local composition model.

My attempt is different. I start from the factorized partition function and use physically sound models for each, keeping the harmony between the parts as much as possible.

I focus to develop group contribution models, because we can use them for calculating thermodynamic data, which have not been measured at all.

The main objective of my thesis was to investigate how the capability of different EOS models change, when we use more complicated physical models. On the other hand I aimed to develop a new group contribution model, which can describe phase equilibria data of non-ideal mixtures containing polar component, by extrapolation from pure component data.

II. Methods

In order to improve the capability of traditional models I treated the terms of the factorised partition function separately, using physically sound models for each, keeping the harmony between the parts as much as possible

I built the models from three parts. For repulsion part I used the following models:
- Carnahan-Starling hard sphere model,
- Boublík and Nezbeda model for molecule with two spherical group,
- Boublík model for chains of fused hard spheres of equal size.

For attraction part I split the dispersion and specific attraction interactions. For dispersive attraction I used:
- van der Waals-Flory random lattice model,
- Alder square well dense gas model.

The specific attraction interaction was described by Smirnova-Victorov quasi-chemical hole lattice model.

Combining the above mentioned parts I developed four EOS variants:
Carnahan-Starling+van der Waals+Smirnova-Victorov   (CS-vdW-SV),
- Boublík-Nezbeda+van der Waals+Smirnova-Victorov   (BN-vdW-SV),
- Boublík-II.+van der Waals+Smirnova-Victorov   (B-II.-vdW-SV),
- Boublík+Alder-Chen-Kreglewski+Smirnova-Victorov   (BACK-SV).

I compared the EOS variants for pure component tension and equilibrium density data of n-alkanes, alpha-ethers and n-alkanols. With the two best EOS I predicted mixture phase equilibria data.

III. New scientific results

1. I developed group contribution method for building molecular parameters of the four EOSs mentioned, using the original Boublík model for alpha non-sphericity parameter. I checked the additivity of the group parameters interpolating for pure component vapor pressure and phase equilibrium density data of homologues. I found that the volume-parameters are additive. The square root of the energy parameter of dispersion attraction part is additive using different ways of normalisation for the different EOSs.

2. Comparing the different group contribution model versions I found that the BN-vdW-SV and the BACK-SV EOS are the best for pure components. The BN-vdW-SV model gives slightly worse results for phase equilibrium liquid density than that obtained with the molecular model, for pure component vapor pressure and vapor density the results are practically the same as with the molecular model. For the BACK-SV model the deviations of the group-contribution models are twice as large as those found with the corresponding molecular model.

3. I developed a new group contribution model for the alpha non-spherically parameter of Boublík repulsion term. The new model describes the molecules as a set of discs with two parameter per functional group. Using the new model I got much better results for description of pure n-alkanes and n-alkanols with BACK-SV EOS, and better results for description of pure n-alcanols with BN-vdW-SV EOS, than those obtained with the original Boublík model. The quality of the results for with the group contribution model for n-alkanes is the same as with BN-vdW-SV and are very close with the BACK-SV EOSs than that for the analogous molecular models.
I listed the values of parameters of new models for CH_3, CH_2 and OH groups.

4. Using the parameters calculated from pure component data I predicted phase equilibria data of mixtures. I compared different mixing rules for repulsive parameters of the two best models, and selected the best mixing rules. For the V^* parameter with the BN-vdW-SV EOS the arithmetic averaging, with the BACK-SV EOS the Lorentz rule gives the best results. For the alpha non-sphericity parameter with the BN-vdW-SV EOS the mixing of geometric parameters, with the BACK-SV the addition with respect to mole fractions gives the best results. I investigated the possible reasons of faults of extrapolation., and made suggestions for development.

IV. Usefulness of results

The two new EOS models can describe phase equilibria of mixtures with similar precision, the average relative deviation of total pressure is about 6-7 %, the average deviation of the vapor concentration is about 2 %.

The BN-vdW-SV EOS has better extrapolation ability, the BACK-SV EOS can describe the pure component data better. At low pressures the BN-vdW-SV EOS, at high pressures and for mixtures including critical components the BACK-SV EOS gives better description.

I compared the ability of the two new EOS models with that of some recently developed group contribution models. I found that my models are not worse, in some cases better for predicting phase equilibria of mixtures than other models, if parameters are estimated from pure component data only.

The results are hopeful, but they will be useful in the daily practice if the parameters will be fine tuned using other thermodynamic data as well (mixture phase equilibria data, V^E).

V. Publications and lectures

A, Publications and lectures in the field of the thesis

Publications
I. Farkas, S. Kemény, É. Thury, A. Deák: Group contribution equation of state model. I. Pure fluids
Hungarian Journal of Industrial Chemistry, 2002, accepted for publication

I. Farkas, S. Kemény, É. Thury, A. Deák, J. H. Son: Group contribution equation of state model. II. Mixtures
Hungarian Journal of Industrial Chemistry, 2002, accepted for publication

S. Kemény, I. Farkas, A. Deák: EOS mixing rules and the quadratic concentration dependence of the second virial coefficient
Fluid Phase Equilibria 128 (1997) 131-135

A. Deák, S. Kemény, I. Farkas: Data driven temperature dependence of EOS parameters
Fluid Phase Equilibria 140 (1997) 97-105

Lectures

Farkas I., Thury É., Csúz E., Kemény S.: Group contribution equation of state model
CHISA'93, Prague, Czech Republic, F2.25 poster, 1993

Farkas I., Kemény S., Deák A., Kovács I.: Group contibution EOS for calculation phase equilibria
Muszaki Kémiai Napok'94, Veszprém, 1994 (in Hungarian)

Farkas I., Kemény S., Thury É., Deák A.: Group contribution equation of state model
13th IUPAC Conference on Chemical Thermodynamics, Clermont-Ferrand, France, 1994

Thury É., Farkas I., Kemény S.: New EOS for modeling strongly non-ideal mixtures.
Muszaki Kémiai Napok'92, Veszprém, 1992 (in Hungarian)

Thury É., Sántha Sz., Farkas I., Deák A.: Calculation with the new EOS for alkane-alkanol mixtures.
6th International IUPAC Worshop and 5th Codata Symposium, Liblice, Czechoslovakia, 1991

B, Other publication

Sawinsky J., Farkas I.: Zero-order reaction in Bingham plastic fluids during laminar flow in an iso-thermal tube rector.
Magyar Kémiai Folyóirat, 99. Évf. 1993. 6. Sz. 247-249 (Hungarian)