

Ph.D. Thesis

**Modelling complex hydrocarbon mixtures using
continuous thermodynamics**

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I. Aims and preliminaries

A mixture containing very many components is called complex mixture. Typical example is the crude oil, its distillation products and residues, products of coal liquefaction, but in wider sense polymers also belong to this category. In my thesis primarily the hydrocarbon and related mixtures were dealt with.

Consideration of the extremely many component of a complex mixture one by one is hopeless, from point of view of both the analysis and calculation of properties, This situation will last in longer term as well in spite of the development of chemical analysis and computers.

Calculation of thermodynamic properties of complex (hydrocarbon) mixtures is very important, as even a rather small saving achieved by more precise model calculations is significant if the large volume of production is considered.

Until about 20 years ago empirical formulae, generalised correlations were almost exclusively used for calculating separation technology and design.

Complex mixtures has been classically characterised by the method of pseudo-components, that is the mixture was separated into several fractions, and each fraction was substituted by a few compounds. From the eighties continuous thermodynamics was applied to modelling complex mixtures. Continuous thermodynamics treats the system as mixture of infinitely many components, the concentration is interpreted as a continuous function of some characteristic parameter, such as molecular mass.

The development of phase equilibrium thermodynamics – especially the appearance of practically useful and relatively simple equations of state and group contribution models – made the development of more sophisticated methods. At the same time the development of methods for chemical analysis - especially that of the spectroscopy – enabled better identification of compounds in fractions, that is better characterisation of fractions.

Complex hydrocarbon mixtures are represented as mixtures of three hydrocarbon homologous families (alkane, aromatic and alicyclic) using the mentioned spectroscopic methods, thus modelling complex mixtures means modelling of these homologous families.

Availability of experimental phase equilibrium and related data in the literature is limited. E.g. vapour pressure data are found for paraffines up to the critical pressure from methane to octane, while less and less of these data are found for compounds with increasing carbon number, available data are farther and farther from the critical pressure. Data for aromatic and alicyclic compounds are even scarcer. In the course of engineering design the phase equilibria are to be modeled at high temperature and high pressure, however. Thus a good model has good extrapolation ability. The most widely used cubic EOS models are not appropriate for this purpose. Therefore a statistical thermodynamically sound group contribution EOS developed by I. Farkas (BME, 2001) was used throughout my work. The first reason of this choice was that causal continuous thermodynamic calculations should unavoidably be based on group contribution models. The second reason was the basically extrapolation nature of the phase equilibrium and engineering calculations for complex mixtures are inevitably of extrapolation type. Thus I had to use a method by

which phase equilibria of mixtures may be predicted far from the temperature and pressure range where the data were measured, and mild empirical fit is required to augment pure component properties.

To estimate the numerous parameters of group contribution equation of state models improved estimation methods were required, considering the rather limited nature of the data base. Thus ridge regression was used, application of which required further development of the method, this became an essential part of my work. The aim of my thesis was estimation of model parameters for homologous series enabling extrapolation capabilities of the model in order to predict phase equilibria properly at high pressure, high temperature and for higher carbon number compounds as well. Another task was to develop the continuous thermodynamic version of the model.

II. Methods

As the model chosen is an equation of state derived through statistical thermodynamics, the parameters are physically sound, and with these parameters the extrapolating ability of the model is good. Thus it was justified to strive for obtaining estimated parameters as close to their true values as possible, instead of obtaining the best fit to the experimental data. This supported the choice of ridge regression instead of method of least squares. Model parameters have been estimated from experimental (literature) thermodynamic data.

The model chosen was used for thermodynamic calculations of both discrete and continuous components, to perform the latter task continuous thermodynamic form of the model had been derived.

III. New scientific results

1. Method of ridge regression known in the literature has been extended.

1.1. I found that the original form (without centering and scaling the variables) is better to use than the widely used correlation form.

1.2. Applying the ridge regression a new unprecedented procedure has been introduced for situations occurring frequently at engineering and scientific models where the model parameters differ from each other by orders of magnitude. The essence of the method is the relative scaling of parameters dividing them by their guessed values before regression. I found these scaled estimates much better than those obtained without scaling. This kind of scaling has been found advantageous even in cases when the guessed values are only very rough estimates.

1.3. I succeeded to prove on the simulation example of a mathematic function and of an equation of state model that the ridge regression is useful not only for linear models but also for non-linear ones.

2. Extrapolation ability of models with least squares and ridge estimated parameters has been compared. Parameters of the BvdW group contribution equation of state model have been estimated from vapour pressure data of n-alkanes for narrower and wider temperature range, and extrapolation calculations were performed. It was found that the model with ridge estimated parameters have better extrapolation ability than that with least squares estimated parameters, both to higher temperature and higher carbon number, for pressure and density as well. This statement is supported by the fact that the ridge estimates with smaller amount of data (spanning narrower temperature range) gave better prediction than least squares estimates based on larger amount of data (from a wider temperature range).

3. Parameters of the BvdW model have been estimated from pure component vapour pressure data for alkanes, aromatics and cycloalkanes.

3.1. It was found that the alkane homologous series are better built of pentane and methylene groups than from methyl and methylene groups, in the latter case unfeasible $\alpha < 1$ values are obtained for pentane and hexane.

3.2. When estimating parameters for the cycloalkane homologous series it is advisable to discard methyl-cyclohexane vapour pressure data because the normal boiling point of this compound is not smoothly fit to the data of others, and the estimated α values are infeasible. Having been discarded the methyl-cyclohexane data the estimated α values will be meaningful (for cyclohexane $\alpha = 1.154$ is obtained). The members of this homologous series are to be built of cyclohexane and methylene groups.

3.3. In the course of building the members of the aromatic homologous series benzene and methylene groups are to be used instead of the aromatic CH- and CH₂-, aliphatic CH₂- and CH₃- groups.

4. The BvdW equation of state with parameters as I estimated was found to be suitable for describing phase equilibria of multicomponent hydrocarbon mixtures, synthetic and real oils, gas condensates.

4.1. The model predicted total pressure of 4 synthetic alkane mixtures containing heavy components up to C₃₀ with high precision. Goodness of prediction was acceptable for boiling pressure for two six-component alkane mixtures.

4.2. Thermodynamic behaviour of synthetic oil containing carbon dioxide was also described with acceptable precision.

4.3. When the BvdW model was compared with traditional models it was found that our model performs significantly better in describing well defined hydrocarbon mixtures (multicomponent mixtures, synthetic oils, where the concentration of components is known)

then the Soave EOS, especially if carbon dioxide is also contained in the mixture. For gas condensates and oils the reliability of the two models is comparable.

4.4. The capability of the BvdW model and those recently proposed in the literature has been compared. I found that the BvdW model gives better results for total pressure of synthetic oils containing heavy compounds up to C_{30} than the LCVW model. The Sanchez-Lacombe model without binary interaction parameters is as good as our model for six-component alkane mixtures.

5. The continuous thermodynamic version of the BvdW model has been developed. For density function to be used instead of mole fractions cubic spline polynomials were used. The low carbon number compounds and gases were treated as discrete components, the larger carbon number compounds were considered as continuous, thus semi-continuous mixtures were used. Ability of the model has been tested on literature examples of paraffinic, paraffinic-naphthenic-aromatic gas condensates and oil mixtures containing permanent gases as well, both in phased equilibria and separation process (flashing). The results were acceptable..

IV. Usefulness of results

The ridge regression method has been only used to linear models (in parameters) in the literature. I succeeded to prove the usefulness and significance of the method for nonlinear systems, such as the Bvdw equation of state. This opens the way of applying ridge regression to other nonlinear models as well.

The BvdW equation of state with parameters as I estimated was found to be suitable for describing phase equilibria of multicomponent hydrocarbon mixtures, both in the context of discrete (traditional) and continuous thermodynamic. It is able to predict modeling phase equilibria and separation processes for hydrocarbon mixtures containing heavy compounds as well. This is essential for modelling deeper exploitation of hydrocarbon content of crude oils.

V. Publications and lectures

S.H. Ngo, S. Kemény, A. Deák: Performance of the ridge regression method as applied to complex linear and nonlinear models, *Chemometrics and Intelligent Laboratory Systems*, 67 69-78 (2003)

S.H. Ngo, S. Kemény, A. Deák: Application of ridge regression when the model is inherently imperfect: a case study of phase equilibrium, *Chemometrics and Intelligent Laboratory Systems*, 72, 185-194 (2004)

Farkas István, Kemény Sándor, Thury Éva, Deák András, Ngo Son Ha:
Group contribution Equations of State model. II Mixtures,
Hungarian Journal of Industrial Chemistry, accepted for publication, 2001

S.H. Ngo, S. Kemény, A. Deák: Capability of a group contribution equation of state for
describing phase equilibria in hydrocarbon systems, Periodica Polytechnica, Ser. Chem.
Eng., accepted for publication, 2005

Ngo S.H., Kemény S., Kollár-Hunek K.: Continuous thermodynamic calculations using
spline polynomials
CHISA'93, Prága, Csehország

Ngo S.H, Kemény S.: Ridge regression for estimating EOS parameters
CHISA'96, Prága, Csehország

Ngo S.H, Kemény S.: Ridge regression for complex linear and non-linear models
Conferentia Chemometrica CC'97, Budapest, 21-23 August 1997

S. H. Ngo, S. Kemény, A. Deák: Is ridge regression better? A case study of phase equilib-
rium, Advances in Chromatography and Electrophoresis – Conferentia Chemometrica,
Budapest, 27-29 October 2003