IV. Modeling of Heat of Mixing of Ethanol + Water System

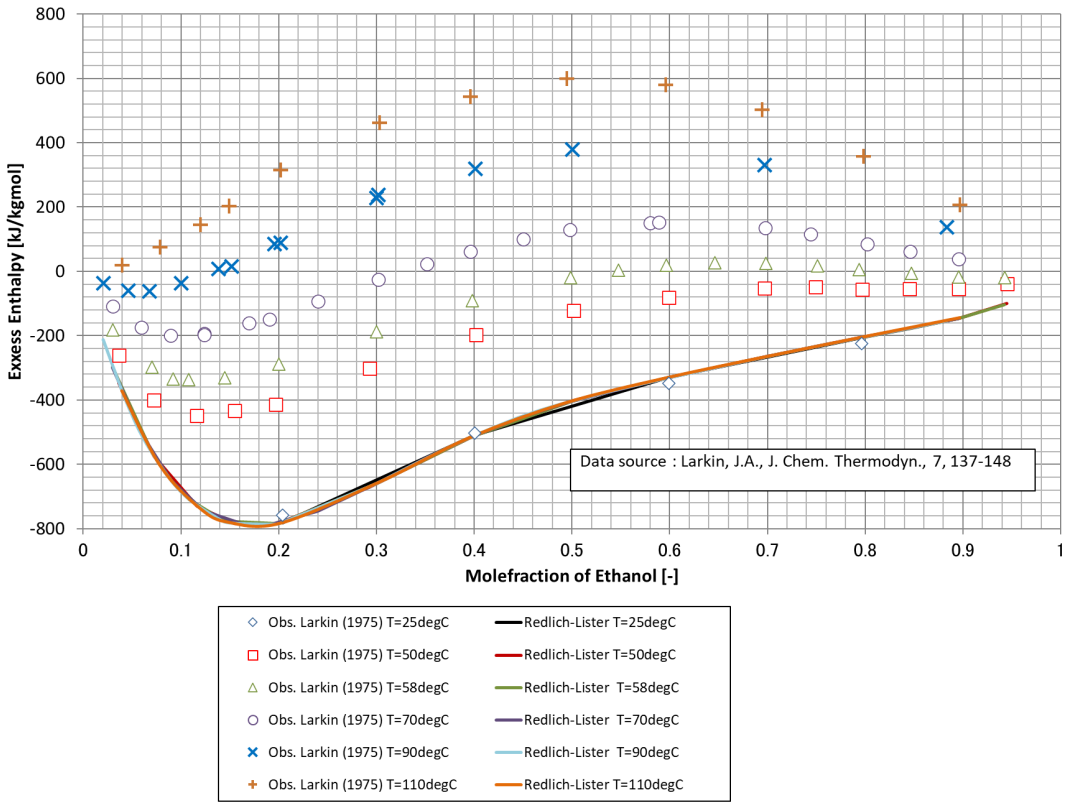
IV-1. Limitation of existing Redlich – Kister model

Redlich-Kister model (RK) is easy to be applied for modeling of heat of mixing. Although RK satisfies Gibbs-Duhem equation, RK is a just simple correlation model and no consideration for temperature dependency.

PRO/II has a tuning parameter set for heat of mixing of Ethanol + Water system.

Fig.3 shows testing results for RK correlation which is existing in PRO/II.

Fig.3 Excess Enthalpy of Ethanol - Water System
Observed Data vs. Redlich-Kister Excess Enthalpy Correlation



As predicted in advance, the existing RK correlation cannot correspond to temperature dependency of the experimental data. The RK correlation of PRO/II is correlated with the experimental data at 25 degC.

The further expansion of RK model is not difficult but easy in order to consider for temperature dependency. However, the existing RK model in PRO/II is useless for modeling of heat of mixing of alcohol + Water system.

IV-2. Modeling of Heat of Mixing of Ethanol + Water System using NRTL and TBC EoS

Generally speaking, liquid activity model (LACT) and equation of state (EoS) are able to be applied for modeling of heat of mixing as well as Redlich-Kister (RK) correlation. RK is just correlation without theoretical background, but LACT and EoS are semi-empirical theoretical model.

Therefore, NRTL which is a popular LACT model and TBC EoS are tested for the modeling in this report. TBC EoS is not popular EoS, but the excess Gibbs energy of the mixing rule is based on NRTL Gibbs free energy.

For correlation work, TDM which is an utility tool of PRO/II is applied.

(1) NRTL

Fig.4 shows correlation results of the experimental data form 25 degC to 110 degC. NRTL shows pretty good correlation results.

The obtained NRTL binary parameters are shown in Fig.4.

Fig.4 Excess Enthalpy of Ethanol - Water System
Observed Data vs. NRTL with tuned parameters based on Excess Enthalpy Data

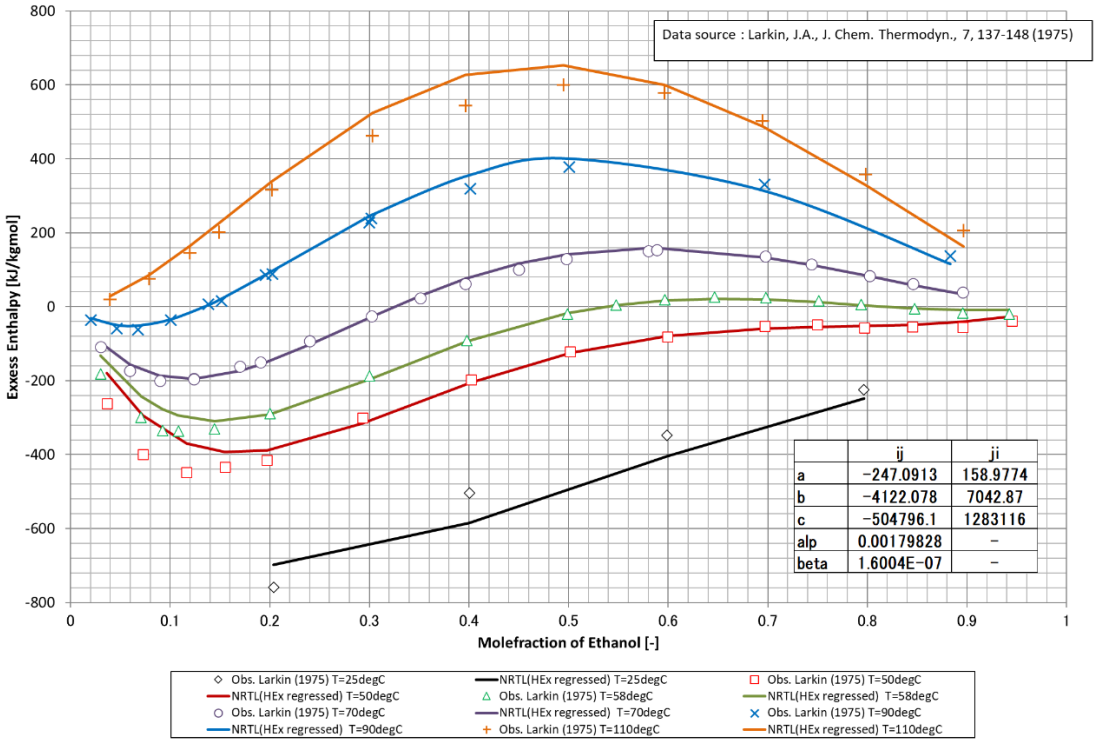
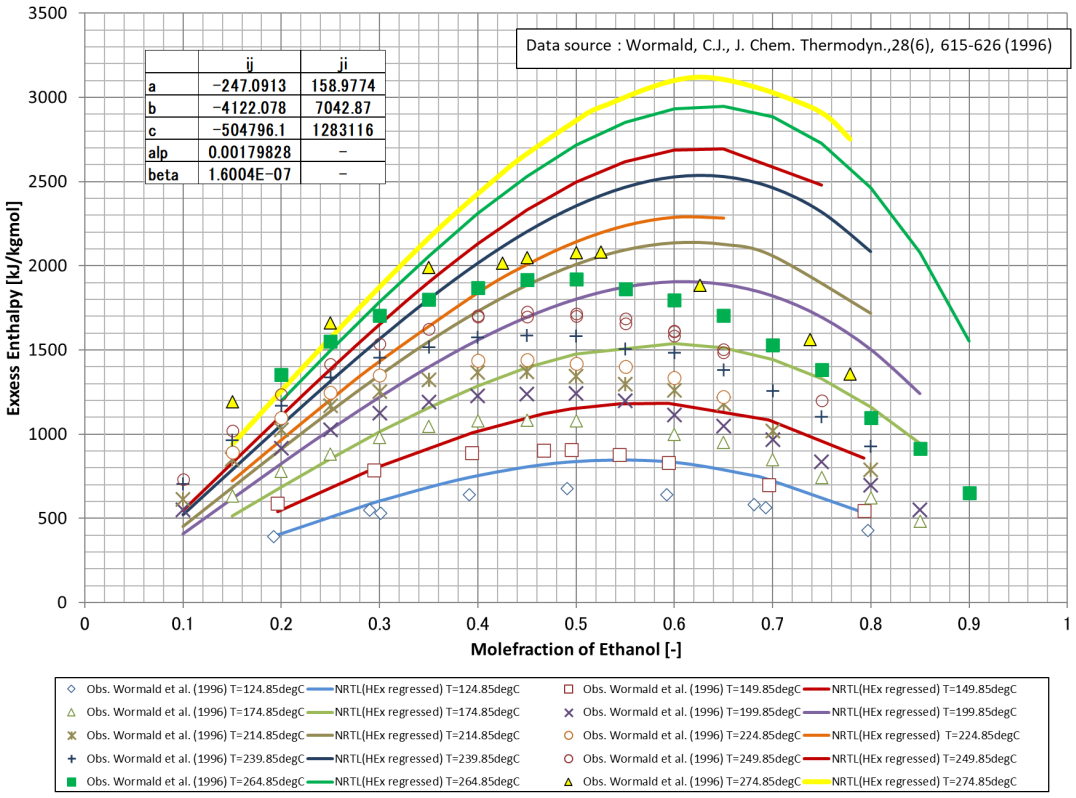


Fig.5 shows predicted results for higher temperature range using NRTL binary parameter set obtained by correlation of the data up to 110 degC. According to Fig.5, significant deviations between the experimental data and predicted results were observed, however at least the endothermic heat of mixing is reproduced by the predicted results.

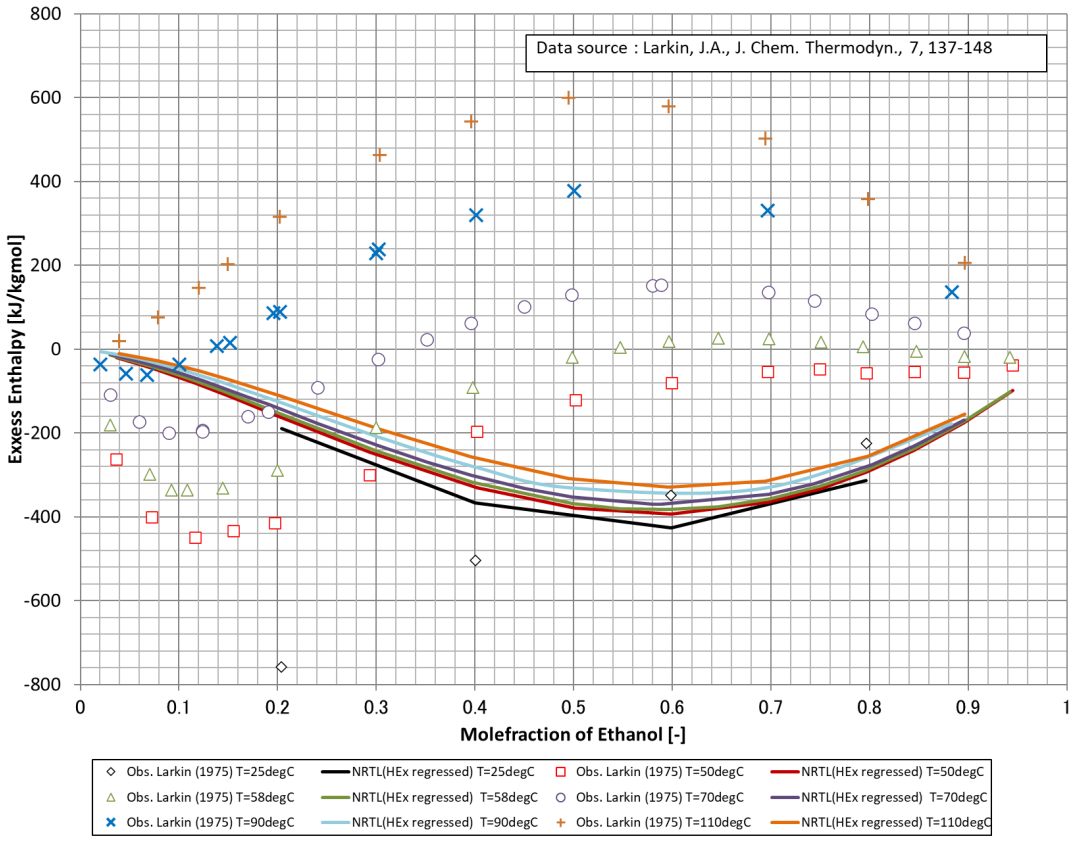
Fig.5 Excess Enthalpy of Ethanol - Water System at 15MPa
Observed Data vs. NRTL with tuned parameters based on Larkin's Data



NRTL is a quite popular model for VLE calculation. Naturally, PRO/II keeps tuned NRTL binary parameter set for VLE calculation of Ethanol + Water system. In Fig.6, this tuned binary parameter set retrieved from SSI DB for VLE calculation was tried to be applied for prediction of excess enthalpy.

As shown in Fig.6, the predicted results were not accepted.

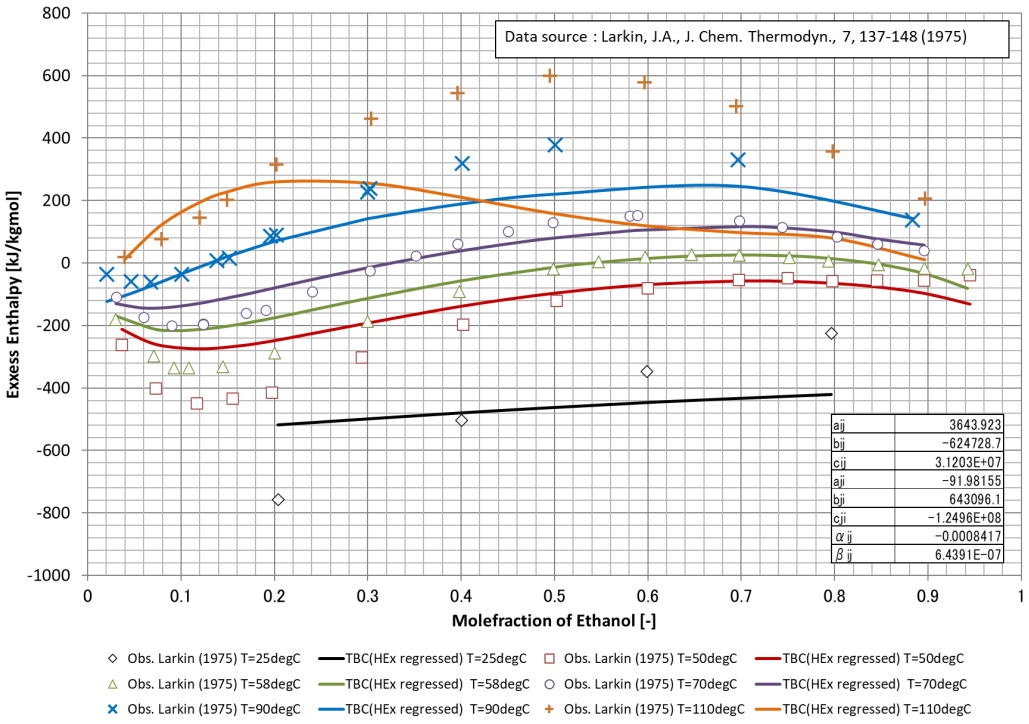
Fig.6 Excess Enthalpy of Ethanol - Water System
Observed Data vs. NRTL with parameters from SSI DB (tuned by VLE Data)



(2) TBC

TBC EoS was applied for correlation. Fig.7 shows correlation results. Unfortunately, good correlation results were not obtained as shown in Fig.7.

Fig.7 Excess Enthalpy of Ethanol - Water System
Observed Data vs. TBC with tuned parameters based on Excess Enthalpy Data



V. Conclusions & Suggestions

Alcohol and Water mixture indicates quite complex behavior in heat of mixing.

PRO/II has provided Redlich-Kister model for modeling of heat of mixing. However, Redlich-Kister was useless for alcohol + Water system according to my validation work.

In contrast, NRTL model was a quite good choice for modeling of heat of mixing of Ethanol + Water system. However, it was not able to get good correlation using TBC EoS and TDM as correlation tool.

According to the framework of existing PRO/II, unfortunately,

1) Even though the liquid activity coefficient (LACT) model which is specified as K value calculation mode is applied for calculation of heat of mixing, PRO/II cannot keep two different binary parameter sets (namely, for instance, one is tuned for VLE and the other is tuned for heat of mixing). Therefore, actually, it is not possible to apply the tuned binary parameter set for calculation of heat of mixing on multi-phase flow sheet simulation.
2) The existing TDM which is an utility tool for parameter regression cannot allow simultaneous regression between phase equilibria (VLE & LLE) and heat of mixing.

As conclusion, the following items are suggestions to further enhancements of PRO/II.

(a) Enhancements of the existing Redlich-Kister

Even though Redlich-Kister is a polynomial equation, it is a simple and flexible fitting model. Therefore, as a further extension, it is easy to introduce temperature dependency parameters to each RK binary parameter. As temperature dependency equation, simple polynomial equation (recommended up to quartic equation, but usually cubic equation is enough) is recommended.

(b) Enhancements of the existing framework for user's choice of LACT model for heat of mixing

As countermeasure, several modification plans can be suggested. But, as simplest solution, I suggest PRO/II to accept unique user choice of liquid activity model with tuned binary parameter sets for model of heat of mixing. This unique user choice shall be independent from choice of thermodynamic model for K value.

(c) Enhancements of TDM

TDM shall accept VLE (and/or LLE) and heat of mixing simultaneously as experimental data set for correlation of LACT model. However, if we focus on alcohol + Water system, my impression is that simultaneous regression between VLE (and/or LLE) and heat of mixing is probably hopeless. However, I think that this improvement on TDM would be useful for other binary system.

Finally, it was my surprise that the existing TDM was easy and smart to find good binary parameter set of NRTL for heat of mixing of Ethanol + Water system. Consequently, I had a quite good impression to TDM.