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# Calculation of excess molar enthalpy of binary liquid mixtures at high pressures from experimental data at low pressures

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ABSTRACT

A new approach for calculating the excess molar enthalpies of binary liquid mixtures at entire pressure range of interest based on the experimental excess molar enthalpy ($H_m^E$) data at low pressure, is proposed. The method is a simple thermodynamic relation combined with the modified Redlich-Kister equation and modified local composition model (NRTL and Wilson) in which the binary parameters were temperature and pressure dependent that are determined by using experimental excess molar volume ($V_m^E$) at different temperatures and pressures. The calculation has been carried out for seven binary systems which include light hydrocarbon-alcohol systems plus water-ethanol. A comparison of the calculated and experimental $H_m^E$ at different temperatures and pressures of seven binary mixtures indicate that the models describe the excess molar enthalpies very well quantitatively.



## 1. Introduction

The excess molar enthalpies of liquid mixtures at high temperature and high pressure (HTHP) are of considerable importance in thermodynamics, while at the same time, it will provide valuable data for testing modern fluid theories [1]. As technology advances, many processes in chemical and petroleum industries increasingly involve high pressure operations, such as gas production, gas separation, coal conversion, heat pumps and high pressure chemical synthesis in which the effect of pressure and of temperature on thermodynamic properties plays an important role [2–5]. Thus, there seems to have been increasing interest in attempting to find that the conventional approach involves an effort to calculate excess molar enthalpy at HTHP. Meanwhile the need for accurate prediction methods for these properties in petroleum industry simulators, in particular in deeper reservoir, where data of high pressure is required, has led to considerable interest in finding out a new modification of local composition (LC) models. Models of this type mostly include one or more adjustable parameters, the values of which must be determined by correlating experimental data.

In this regard, a number of researchers tried to find best modification of models and then utilized them for predictions. Nagata and Yamada [6] assumed that the binary parameters of the Wilson, Hell and NRTL models were linearly temperature-dependent. Also they successfully cross-correlated excess Gibbs free energy and excess enthalpy from both experimental data simultaneously. Vonka et al. [7] revealed that the correlating of excess molar enthalpy through temperature-dependent parameters of Wilson and NRTL models to predict the VLE data, was not always successful. Skjold-Jørgensen and coworkers [8,9] were seeking to modify the models, as these models fail to give a satisfactory result to describe the properties of the excess Gibbs energy and excess enthalpy of mixing. To help achieve this objective, they assumed the reciprocal temperature and composition function of interaction parameters of the UNIQUAC/UNIFAC models and obtained good results for several systems. Different from those already mentioned, Chatterjee et al. turned to calculate the enthalpy departures at high pressure and temperature by means of Lenoir's compressibility charts [2]. With regard to the relationship between excess enthalpy and excess volume, two different research tasks are performed. One was done by Hansen and Eckert [10] wherein they express the relationship between $H^E$ and $V^E$ based on the thermodynamic relations. and the other, which is slightly similar to our work, is a study conducted by Siddiqi and Lucas [3]. They sought to find temperature and pressure dependence of the relation between $H^E$ and $V^E$. The studies reported by Demirel and coworkers [11], assuming non-linear temperature dependence of interaction parameters. They also correlated $H^E$ data with the NRTL

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**Nomenclature**

| | |
|---|---|
| $A_i$ | adjustable parameters of Redlich-Kister equation |
| $c_{i,j,k}$ | adjustable coefficients of Redlich-Kister equation |
| $G_m^E$ | excess molar Gibbs's free energy |
| $H_m^E$ | excess molar enthalpy in J/mol |
| $V_m^E$ | excess molar volume |
| T | temperature in K |
| P | pressure in MPa |
| R | Universal gas constant in J/mol/K |
| $\Delta\lambda_{12}$, $\Delta\lambda_{21}$ | interaction energy parameters in *Wilson* model |
| $\Delta g_{12}$, $\Delta g_{12}$ | interaction energy parameters in *NRTL* model |
| $C_{ij}$, $D_{ij}$ | adjustable coefficients of interaction parameters in *Wilson* and *NRTL* model |
| $x_i$ | mole fraction of component *i* |
| M | modified |
| AAD | average absolute deviation |
| NDP | number of data point |

*Greek letters*

| | |
|---|---|
| $\alpha_{12}$ | non-randomness parameter in *NRTL* model |
| $\sigma$ | standard deviation |

*Subscripts*

| | |
|---|---|
| exp | experimental |
| cal | calculated |
| i | initial state |
| f | final state |

*Superscripts*

| | |
|---|---|
| E | excess |

and UNIQUAC models for 44 binary mixtures. Shen and Nagata [4,12] introduced a new method to predict the excess enthalpy from infinite dilution activity coefficients at different temperatures. All of them showed that this approach could successfully predict $H^E$ for binary systems. In a study reported by Huang and Lee [13], a new modified Wilson models was applied to simultaneously estimate the excess enthalpy, excess Gibbs energy and VLE data. Two temperature-dependent forms, linear and non-linearly reciprocal, were considered by them. They made a comparison between their modified model and other modifications. In a recent study, Escandell et al. [14] presented a new formulation of NRTL along with temperature and composition dependent mixing rules and new interaction parameters. In addition to the studies above, a number of studies have been performed to scientifically predict the excess enthalpy at HTHP using an equation of state. For example, in the research that has been done by Casielles et al. [15] or Dai et al. [16], used PR EoS for their correlation. Other researchers employed an EoS-$G^E$ model to calculate the excess enthalpy, especially one that was carried out by Matsuda et al. [5], in which, based on $H^E$ data at ambient condition, the $H^E$ values at HTHP, were predicted. They combined PR EoS with NRTL model to calculate the excess molar enthalpy. Some investigations have been done on testing EoS-$G^E$ model for prediction of $H^E$ [17], although they have tried to predict $H^E$ at low and high pressure.

The summary description of research work performed by several researchers confirms that the modification of local composition model, presuming temperature or occasional composition dependence of interaction parameters, surely improves the preciseness of either simultaneous correlation of cross-prediction.

In this study, the LC models and Redlich-Kister equation were modified by expressing the binary parameters as a function of temperature and pressure to improve the accuracy and ability of spontaneous correlation of experimental data at different pressures and temperatures. Sometimes, the calculations done with this kind of modified model are worse than those with the original models because the additional adjustable parameters result in more uncertainties in the determination of model parameters than with a model having fewer adjustable parameters [4].

In principle, the aim of the present investigation is to introduce a new approach for calculating $H_m^E$ for binary systems at any given pressure on the basis of $H_m^E$ experimental data at lower pressure by utilizing the $V_m^E$ experimental data at different temperatures and pressures and two kinds of modified local composition models (NRTL and Wilson) and Redlich-Kister equation. Generally, these models involve two or more adjustable parameters which, in this study, defined as a temperature and pressure dependent polynomial and the values of which must be determined by curve fitting of $V_m^E$ experimental data. This method has been tested by calculating $H_m^E$ for seven binary systems consisting of alcohols, alkanes, alkenes and water [18–23]. The systems have been chosen based on the available experimental data in the literature.

## 2. Theoretical framework

Usual to almost all derivations of $V_m^E$ and $H_m^E$ from Gibbs free energy models is the supposition of pressure and temperature independence of the parameters, although this is not severely true hypothesis. It is today accepted that the binary parameters of LC models depend on temperature and some pressure, in particular, in mixtures encountered in the petroleum and gas processing industries. Therefore, this study is attempted to extend an expression to binary parameters of Wilson and NRTL models from the original version, in which, for the first time the temperature-pressure dependence has been introduced in the best feasible way. We have found, however, that if the parameters expressly somehow depend on temperature and pressure, predictive capability of the models will improve. However, a model describing the interrelation between $V_m^E$ and $H_m^E$ accurately by means of temperature-pressure dependent binary parameters would be very interesting since the parameters of fitting could be estimated from data of $V_m^E$ at different temperatures and pressures.

It is assumed that the calculation process can be described in two steps:

(1) Correlate the excess molar volume experimental data with semi empirically temperature and pressure simultaneous dependence of parameters
(2) Calculate the excess molar enthalpies from available measurements of excess molar volumes at any condition using merely thermodynamic relation;

### 2.1. Correlation of experimental data

As mentioned above, the focus of the present work is to calculate the excess molar enthalpy for the binary mixtures on which the experiments of excess molar volume covering a range of temperatures and pressures were performed. In this approach three models are turned to correlate the excess molar volume