Korean J. of Chem. Eng., **13**(2), 115-122 (1996)

MODIFIED RESPONSE SURFACE METHODOLOGY (MRSM) FOR PHASE EQUILIBRIUM-THEORETICAL BACKGROUND

Jong-Chul Park†, Dong-Myeong Ha* and Moon-Gab Kim**

Dept. of Chem. Eng., Kyung Hee University, Suwon 449-701, South Korea
*Dept. of Industrial Safety Eng., Semyung University, Jecheon 390-230, South Korea
**Dept. of Chem. Eng., Sang Ju National Polytechnic University, Sangju 742-170, South Korea

(Received 29 September 1994 • accepted 22 August 1995)

Abstract – The effect of molecular interaction energy among different molecules in the mixed solutions significantly depends upon the size of individual molecule size and molecular arrangement. In order to compensate these effects on the existing method, a new method of representing the relationship of temperature and compositions of each phase (vapor and liquid phases in equilibrium) and azeotropic mixture is proposed. The optimized models of the RSM (response surface methodology) and MRSM (modified response surface methodology) are briefly described. The applications of these models to the solution thermodynamics are also explained.

Key words: *Modified Response Surface Methodology, Statistical Molecualr Thermodynamics, Advanced Computer Simulation Engineering, Cacoon-type Quaternary Azeotropic Mixture, Multiple Parameters Multiple Terms (MPMT) Equations*

INTRODUCTION

Studies on the nonidealities of solution thermodynamics and vapor-liquid equilibria of mainly binary and ternary systems have been conducted by many scholars and results are reported in various published journals [King, 1969; Gmehling et al., 1981; Prausnitz et al., 1986; Reid et al., 1987].

However, such studies have been undertaken mainly for binary and ternary systems. Furthermore, theoretical investigation and representation methods of equilibria of vapor-liquid phases beyond ternary are few and can be regarded as an unexplored case.

Various equations to estimate the thermodynamic properties of chemical solution have been proposed, such as TPTT (two parameters two terms) equations: Margules [King, 1969], van Laar [Prausnitz, 1986], Wilson [Wilson, 1964], NRTL [Renon and Prausnitz, 1968], ASOG [Kojima and Tochigi, 1979], UNIQUAC [Abram and Prausnitz, 1975] and UNIFAC [Fredenslund et al. 1979] etc., MPMT (multiple parameters multiple terms) equations: Redlich-Kister [Redlich-Kister, 1948], Wohl [King, 1969], Lu-Li Ting [Lu-Li Ting, 1959], Chao-Hougen [Chao-Hougen, 1958] and Nagata [Nagata, 1962], TCR (temperature-composition relationship) equations of Malesinski [Malesinski, 1965], Hilm [Hilm et al., 1970], Wisniak-Tamir [Wisniak-Tamir, 1977] and Hu [Hu, 1994].

Previously reported results of comparative studies of these methods by various investigators [Park, 1977, 1979, 1982, 1985, 1986; Lee and Starling, 1985] indicated that a further study of compensating non-ideality is required, based on chemical solution theory of polymerization and association due to hydrogen bond, and statistical molecular thermodynamics due to different molecular size and various configuration among molecules, molecular interaction energy between similar and different molecules [Lee and Starling, 1985; Lee, 1988; Park, 1979, 1982, 1986, 1988].

Current theoretical study of the solution theory has made significant advances. The progress is chiefly due to the studies of

(1) molecular theories based on statistical molecular thermodynamics

(2) numerical simulation of molecular movements by advanced computer simulation engineering

(3) scattering experiments with X-ray, neutrons, etc.

Previous studies conducted by numerous scholars also indicated that the Wilson's parameters (or TPTT's parameters) are not constants but varies depending on a composition of the mixed solutions and data sources of the parameter estimations [Lee, 1985; Park, 1977, 1979, 1982, 1986]. Statistical analysis of many binary mixed solutions clearly demonstrated that the range of variation of these parameters g_{12}-g_{11} & g_{21}-g_{22} and molecular interaction energy parameters g_{12} & g_{21} are more than significant beyond the range of the expected experimental errors [Park, 1977, 1979, 1982, 1986].

Recent development of statistical molecular thermodynamics are briefly described. The theoretical backgrounds of the newly proposed Modified Response Surface Methodology (MRSM) are also explained. This new method of finding a type, composition and temperature of the multicomponent azeotropic mixtures (particularly ternary and quaternary) is also found to be extremely useful [Park, 1983, 1985, 1987, 1988, 1990, 1991, 1992].

STATISTICAL MOLECULAR THERMODYNAMICS AND PARAMETER ESTIMATION

1. Parameter Correlation

The published vapor-liquid equilibrium data of several binary systems were carefully screened by the statistical and thermodynamic methods known to us [Gmehling et al., 1981; Reid et al., 1987]. Then, a few were selected for the purpose of this study. Individual experimental points of a data set were regressed by means of the Wilson formular and two parameters were estimated

---

†Author to whom correspondence should be addressed.

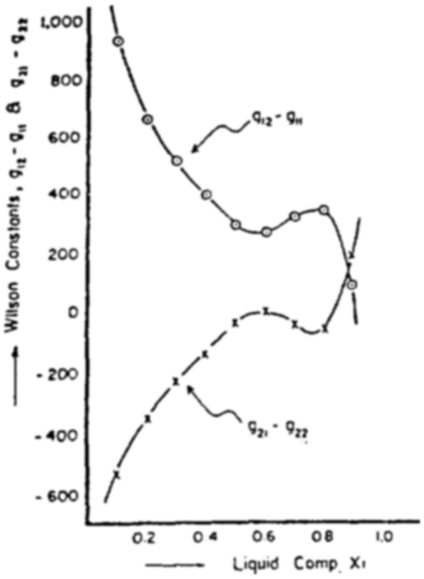

Fig. 1. Wilson constant parameters g_{12}-g_{11} & g_{21}-g_{22} vs. liquid composition x_1 for the system of benzene(1)-cyclohexane(2).

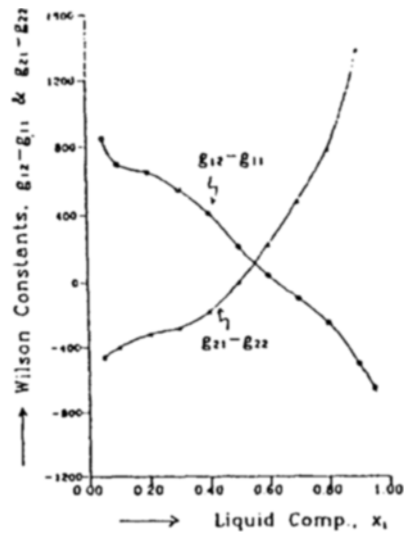

Fig. 2. Wilson constant parameters g_{12}-g_{11} & g_{21}-g_{22} vs. liquid composition x_1 for the system of methyl acetate(1)-benzene(2).

at different temperatures and composition of each data set. Series of the regressed pair g_{12}-g_{11} & g_{21}-g_{22} vs. liquid composition x_1 of the system of benzen(1)-cyclohexane(2) are plotted on Fig. 1 and of the system of methyl acetate(1)-benzene(2) on Fig. 2.

From these results, the molecular interaction parameters (or pair correlateion function) g_{12} & g_{21} are estimated and the estimated values of g_{12} & g_{21} vs. liquid composition x_1 for the system of methyl acetate(1)-benzene(2) are plotted on Fig. 3.

From the results of this study, it has been demonstrated that the TPTT parameters g_{12}-g_{11} & g_{21}-g_{22} and the parameters g_{12} & g_{21} are not constant, but change with composition of the mixed solutions as shown on Fig. 1, 2 and 3 [Park, 1977, 1979, 1982, 1986, 1988, 1992].

The variation of these parameters throughout a whole composition range makes an estimation of the parameters applicable for an entire composition range rather difficult on the contrary to the previously accepted assumption that the values of only two constant parameters (Wilson's or TPTT's) are required for the individual mixed solutions. Various methods of finding a correlation between two Wilson's parameters g_{12}-g_{11} & g_{21}-g_{22} had been attempted by Park [Park, 1979, 1988, 1992]. Among these studies, a plotting of two parameters on X-Y coordinate (g_{12}-g_{11} vs g_{21}-g_{22}) had shown to be the most reasonable correlation between two parameters. The plotting of each points which represent the regressed pairs of individual experimental points on the X-Y coordinates are connected to be shown as locus of parabolas for five different binary mixtures; methyl acetate-cyclohexane, benzene-cyclohexane, ethanol-benzene, benzene-n-heptane and n-heptane-ethanol on Fig. 4, similarly, g_{12} vs. g_{21} for three different binary mixtures; methyl acetate-benzene, methyl acetate-cyclohexane, benzene-cyclohexane on Fig. 5 [Park, 1977, 1979, 1986, 1988, 1992]. Similar correlations of the Wilson, NRTL and UNIQUAC parameters are also made for six different binary mixtures, and the results are reported [Shin and Park, 1988].

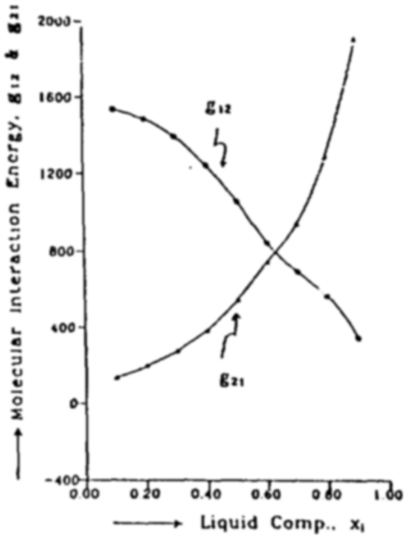

Fig. 3. Molecular interaction energy parameters, g_{12} & g_{22} vs. liquid composition x_1 for the system of methyl acetate(1)-benzene(2).

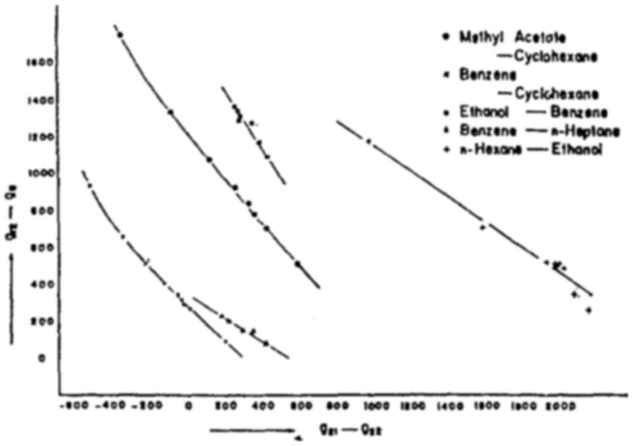

Fig. 4. Correlation of the Wilson constant parameters g_{12}-g_{11} vs. g_{21}-g_{22} for five different binary systems.

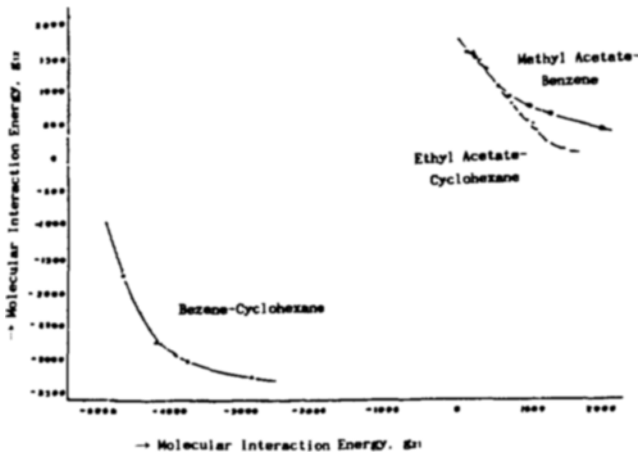

Fig. 5. Correlation of the molecular interaction energy parameters, g_{12} vs. g_{21} for three different binary systems.

2. Statistical Molecular Themodynamics

Analysis of variation of the TPTT parameters versus composition, molecular size and molecular interaction energy of the solution based on statistical molecular thermodynamics has been reported [King, 1969; Lee and Starling, 1985; Park, 1979, 1982, 1986, 1991a, 1991b]. Based on these studies, the TPTT parameters are function of the molecular interaction parameters (the pair correlation functions) $g_{ij}(r)$ which is dependent on the temperature, density and composition of the mixed solutions [Lee, 1988; Park, 1979, 1986, 1988].

When the equation of state developed for a pure substance is extended to mixtures, one of the important questions is the composition dependence of the new equation. This dependence, in practice, is incorporated into the equation through mixing rules applied to the reduced state variables and the parameters of the equation [Lee, 1988; Park, 1988].

The equation of state for binary mixture, mixture of N_A molecules of type A and N_B molecules of type B is expressed in terms of the pair potentials U_{ij} and molecular pair correlation function (pcf) g_{ij} as

$$\frac{P}{\rho\kappa T}=1-\frac{\beta\rho}{6}\sum_i\sum_j x_i x_j\int dr\, r\frac{\partial U_{ij}}{\partial r}g_{ij}(r,\ \rho,\ T,\ \mathbf{X}) \tag{1}$$

Attempts have been made to approximate the above equation by the van der Waals n-fluid theories (i.e., one-fluid, two-fluid, and three-fluid theories), where the composition dependence is simplified and the $g_{ij}(r)$ are evaluated at reduced states characterized by the energy ε_x and size parameters σ_x. The assumptions made in the n-fluid theories are on the relations between the mixture $g_{ij}(r)$ and pure $g_o(r)$. The mixture pair correlation function, $g_{ij}(\mathbf{X})$ are function of mixture composition $\mathbf{X}=(x_A,\ x_B)$, but pure $g_o(r)$ are not.

$$g_{ij}\left(\frac{r}{\sigma_{ij}};\ \rho,\ T,\ \mathbf{X}\right)=g_0\left(\frac{r}{\sigma_x};\ \rho\sigma_x^3,\ \frac{\kappa T}{\varepsilon_x}\right)$$
$$\sigma_x^3=\sum_i\sum_j x_i x_j\sigma_{ij}^3$$
$$\varepsilon_x\sigma_x^3=\sum_i\sum_j x_i x_j\ \varepsilon_{ij}\sigma_{ij}^3 \tag{2}$$

By these approximation, the composition dependence in g_{ij} is substituted by equating g_{ij} to the pure fluid g_0 [Lee, 1988].

The liquid theory of local compositions explains that the nearest-neighbor number, $N_{AB}(L)$ of B molecules surrounding a central A molecule within a sphere of radius L is

$$N_{AB}(L)=\rho_A\int_0^L dr\ 4\pi r^2\cdot g_{AB}(r) \tag{3}$$

$$X_{BA}=\frac{N_{BA}(L_{BA})}{N_{AA}(L_{AA})+N_{BA}(L_{BA})}$$
$$=\frac{x_B\int_0^{L_{BA}}dr\ 4\pi r^2\cdot g_{BA}(r)/\int_0^{L_{AA}}dr\ 4\pi r^2\cdot g_{AA}(r)}{x_A+x_B\int_0^{L_{BA}}dr\ 4\pi r^2\cdot g_{BA}(r)/\int_0^{L_{AA}}dr\ 4\pi r^2\cdot g_{AA}(r)} \tag{4}$$

Comparing with the equations of Wilson for the local compositions [Lee, 1988; Park 1988].

$$x_{BA}=\frac{x_B\Lambda_{BA}}{x_A+x_B\Lambda_{BA}} \tag{5}$$

$$\Lambda_{BA}=\frac{\int_0^{L_{BA}}dr\ 4\pi r^2\cdot g_{BA}(r)}{\int_0^{L_{AA}}dr\ 4\pi r^2\cdot g_{AA}(r)} \tag{6}$$

Furthermore, we could rewrite the pair correlation function $g_{ij}(r)$ in terms of the potentials of mean force.

$$\int_0^{L_{BA}}dr\ 4\pi r^2\cdot g_{BA}(r)=\int_0^{L_{BA}}dr\ 4\pi r^2\ \exp[-\beta\overline{W}_{BA}(r)]$$
$$=V_{BA}\cdot\exp[-\beta W_{BA}(r)] \tag{7}$$
$$V_{BA}=\frac{4}{3}\pi\ L_{BA}^3,$$

$\overline{\overline{W}}_{ij}(r)$: potential of mean force force evaluated at some mean location in the region of integration

$$\Lambda_{BA}=\frac{V_{BA}}{V_{AA}}\exp[-\beta(\overline{W}_{BA}-\overline{W}_{AA})] \tag{8}$$

The pair correlation functions $g_{AA}(r)$, $g_{AB}(r)$, $g_{3B}(r)$ and the potential of mean force $W_{BA}(r)$, $W_{AA}(r)$ are all composition dependent. The parameters Λ_{ij} are also composition-dependent [Lee, 1988; Park, 1988].

TPTT (or Wilson) parameters g_{12}-g_{11} and g_{21}-g_{22} as shown on Fig. 1, 2 [Chao and Hougen, 1958; Nagata, 1962], and the molecular interaction parameters g_{12}, g_{21} of Fig. 3 show the variation of these parameters with liquid composition, x_1 of the mixed solutions [Park, 1988].

3. Parameter Estimation and Model Selection

In general, any systems of chemical processes can be expressed by the following mathematical equation relating the expected values of a response η to the experimental variables $x_1,\ x_2,\ \cdots,\ x_p$,

$$\eta=f(\beta_1,\ \beta_2,\cdots,\beta_p;\ x_1,\ x_2,\cdots,x_p) \tag{9}$$

Where $\beta_1,\ \beta_2,\cdots,\beta_p$ are the parameters of the system [Box, 1954; Hill and Hunter, 1966].

Under the standard statistical assumption the dependent variable η can be given by the following linear-one-parameter model with a matrix notation

$$\eta=\mathbf{X}\boldsymbol{\beta} \tag{10}$$

Where, for the same dependent variable measured n times the dimension of η are $[n\times 1]$ and those of variable vector $\mathbf{X}$ are $[n\times p]$. The parameter vector $\boldsymbol{\beta}$ is $[p\times 1]$.

Thus, we have

$$\boldsymbol{\eta}=\begin{bmatrix}\eta_1\\ \eta_2\\ \vdots\\ \eta_n\end{bmatrix} \tag{11}$$

$$\mathbf{X}=\begin{bmatrix}x_{11} & x_{12} & \cdots & x_{1p}\\ x_{21} & x_{22} & \cdots & x_{2p}\\ \vdots & \vdots & & \vdots\\ x_{n1} & x_{n2} & \cdots & x_{np}\end{bmatrix} \tag{12}$$

$$\boldsymbol{\beta}=\begin{bmatrix}\beta_1\\ \beta_2\\ \vdots\\ \beta_p\end{bmatrix} \tag{13}$$

As the expected values of unbiased estimations **Y** and **b** are

$$\mathbf{Y}=\eta(\mathbf{X},\ \beta)+\varepsilon=\beta\mathbf{X}+\varepsilon \tag{14}$$

$$E(\mathbf{Y})=\eta \tag{15}$$

$$E(\mathbf{b})=\beta \tag{16}$$

$$\mathbf{b}=[\mathbf{X}^T\mathbf{X}]^{-1}\ [\mathbf{X}^T\mathbf{Y}] \tag{17}$$

where $\mathbf{X}^T$ is transpose of the matrix **X**, and $[\mathbf{X}^T\mathbf{X}]^{-1}$ for the inverse of the matrix $[\mathbf{X}^T\mathbf{X}]$.

When information regarding the measurement error is present and σ_i^2 is far from constant (or non constant variance), the maximum likelihood method can be used.

$$\mathbf{b}_{ML}=[\mathbf{X}^T\phi^{-1}\mathbf{X}]^{-1}\mathbf{X}^T\phi^{-1}\mathbf{Y} \tag{18}$$

$$\mathbf{S}_{ML}=[\mathbf{Y}\text{-}\mathbf{X}\beta]^T\phi^{-1}[\mathbf{Y}\text{-}\mathbf{X}\beta] \tag{19}$$

Then, the covariance of $\mathbf{b}_{ML}$ is

$$\mathrm{Cov}(\mathbf{b}_{ML})=[\mathbf{X}^T\phi^{-1}\mathbf{X}]^{-1} \tag{20}$$

Covariance matrix of the observation errors ϕ is

$$\phi=\sigma^2\Omega \tag{21}$$

where $\boldsymbol{\Omega}$ is known part of ϕ where σ^2 is unknown and σ^2 is variance of observation errors

then,

$$\mathbf{b}_{ML}=[\mathbf{X}^T\Omega^{-1}\mathbf{X}]^{-1}\ [\mathbf{X}^T\Omega^{-1}\mathbf{Y}] \tag{22}$$

$$\mathbf{S}_{ML}=\sigma^{-2}\ [\mathbf{Y}\text{-}\eta]^T\Omega^{-1}\ [\mathbf{Y}\text{-}\eta] \tag{23}$$

$$\mathbf{R}_{ML}=(\mathbf{Y}\text{-}\bar{\mathbf{Y}})^T\Omega^{-1}(\mathbf{Y}\text{-}\bar{\mathbf{Y}}),\ \bar{\mathbf{Y}}=\mathbf{X}\ \mathbf{b}_{ML} \tag{24}$$

where $\mathbf{b}_{ML}$ is a parameter matrix of the multiple regression,
$\mathbf{S}_{ML}$ is the maximum likelihood sum of squares, and
$\mathbf{R}_{ML}$ is the maximum likelihood residual sum of squares

PROPOSED NEW METHODOLOGY

1. Response Surface Methodology (RSM) Model

RSM (response surface methodology) which has been used as an optimization method of statistics has been adapted [Park, 1979, 1983, 1985, 1987] and modified for our purpose as a new method to express the relationship of temperature T and composition x_1, x_2, x_3 (or $x_3=1-x_1-x_2$) of the mixed solution of liquid phase and y_1, y_2, y_3 (or $y_3=1-y_1-y_2$) of the vapor phase. This method is also used to predict a type, temperature and composition of the azeotropic mixtures of ternary and quaternary systems. The graphic contours can be obtained by computer garaphics in the triangular coordinate for ternary and tetrahedron for quaternary [Park et al., 1990, 1992; Kim et al., 1995].

Table 1. RSM models

Model no.	Model formular	No. of parameters
1	$T=a+bx_1+cx_2+dx_1^2+ex_2^2$	5
2	$T=a+bx_1+cx_2+dx_1^2+ex_2^2+fx_1x_2$	6
⋮	⋮ ⋮	⋮
7	$T=a+bx_1+cx_2+dx_1^2+ex_2^2+fx_1x_2$ $+gx_1^2x_2+hx_1x_2^2+kx_1^2x_2^2+lx_1^3+mx_2^3$	11
⋮	⋮ ⋮	⋮
12	$T=a+bx_1+cx_2+dx_1^2+ex_2^2+fx_1x_2$ $+gx_1^2x_2+hx_1x_2^2+kx_1^2x_2^2+lx_2^3+mx_1^2x_2^2$ $+nx_1^3x_2+px_1x_2^3+qx_1^4+rx_2^4$	15

Table 1 shows four (4) models of twelve to correlate the temperature with solution composition. Individual models are fitted with previously published experimental data in various journals [Chao and Hougen, 1958; Nagata, 1962] by multiple regression method [Park, 1977, 1983, 1985, 1987].

The statistical method adapted is briefly described above by matrix notation, and the estimated parameters are shown by β matrix [Box, 1945; Hill and Hunter, 1966]. The model selection of the best fitting was performed by the maximum likelihood method and statistical analysis of variance (ANOVA). The finally selected model for this purpose is called RSM model and is shown as the Eq. (27) for ternary systems.

The final equations of the estimated parameters for ternary system of ethyl acetate(1)-benzene(2)-cyclohexane(3) [Chao and Hougen, 1958] for vapor and liquid phases are shown as the Eq. (25) of vapor phase and the Eq. (26) of liquid phase.

Vapor phase:

$$\begin{aligned}T=\ &82.7854-42.7389y_1-19.5076y_2+45.0135y_1^2+20.3635y_2^2\\ &+63.8495y_1y_2-22.110y_1^2y_2-17.7043y_1y_2^2+6.34787y_1^2y_2^2\\ &-7.18502y_1^3-3.2630y_2^3\end{aligned} \tag{25}$$

Liquid phase:

$$\begin{aligned}T=\ &78.9092-30.2648x_1-4.10856x_2+34.0256x_1^2+0.0809658x_2^2\\ &+18.3108x_1x_2+3.75410x_1^2x_2+14.2123x_1x_2^2+11.1745x_1^2x_2^2\\ &-6.36677x_1^3+5.27023x_2^3\end{aligned} \tag{26}$$

It was found that some systems which behave closely like an ideal system, can be fitted with a simple model such as model 1 or 2 of Table 1 [Park, 1983] or model shown as the Eq. (27) for quaternary system [Park, 1985, 1988].

$$\begin{aligned}T=\ &a+bx_1+cx_2+dx_1^2+ex_2^2+fx_1x_2+gx_1^2x_2+hx_1x_2^2+kx_1^2x_2^2\\ &+lx_1^3+mx_2^3\end{aligned} \tag{27}$$

By computer graphics technique, the response surfaces of liquid and vapor phases for ternary system of ethyl acetate-benzene-cyclohexane are shown as Fig. 6 and 7 [Park, 1979, 1983, 1985, 1987].

2. Modified Response Surface Methodology (MRSM) Model

The RSM model has been further modified for general application of ternary and quaternary-this is the MRSM model. This methodology estimates the equilibria temperature of the system

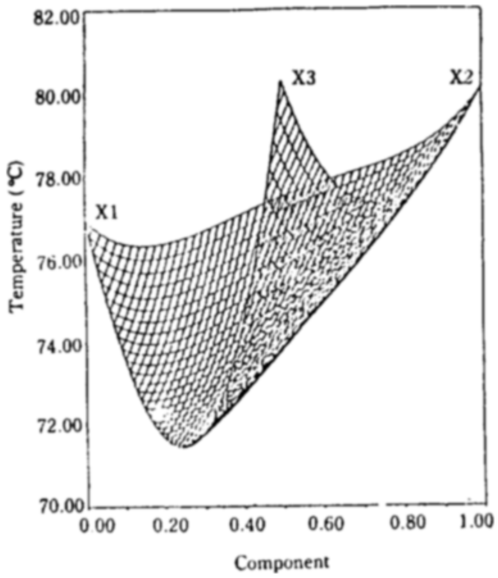

Fig. 6. Response surface of ternary system, ethyl acetate(1)-benzene (2)-cyclohexane(3), data source: K. C. Chao & O.A. Hougen (liquid phase).

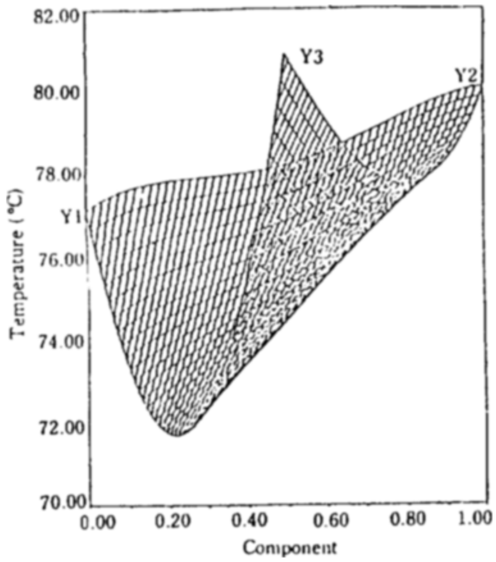

Fig. 7. Response surface of ternary system, ethyl acetate(1)-benzene (2)-cyclohexane(3), data source: K.C. Chao & O.A. Hougen (vapor phase).

from the known phase compositions of the N components system directly without experimental data. This methodology should provide an information of the possible azeotropic formation on liquid and vapor phases (type, composition & temperature) in ternary and quaternary systems. Actual application of this method for ternary and quaternary systems is well described in the previous publications of this series "Modified Response Surface Methodology (MRSM) for Phase Equilibrium-Application" [Park et al., 1990; Park, 1992; Kim et al., 1995].

The individual independent variables x_1, x_2, x_3, $\cdots$ x_i, x_j, $\cdots$ x_p for liquid phase, y_1, y_2, y_3, $\cdots$ y_i, y_j, $\cdots$ y_p for vapor phase and the interactions between independent variables such as x_1x_2, x_1x_3, x_2x_3, $\cdots$, $x_i^m x_j^n$ & y_1y_2, y_1y_3, y_2y_3, $\cdots$, $y_i^m y_j^n$ are related to the phase temperature T as MRSM-1 and MRSM-2 models [Park et al., 1990; Ha and Park, 1991].

MRSM-1 model:

$$T=\Sigma T_ix_i+\Sigma\Sigma A_{ij}x_ix_j+\Sigma\Sigma B_{ij}x_ix_j(x_i-x_j) \text{ (liquid phase)}$$
$$T=\Sigma T_iy_i+\Sigma\Sigma A'_{ij}y_iy_j+\Sigma\Sigma B'_{ij}y_iy_j(y_i-y_j) \text{ (vapor phase)} \tag{28}$$

MRSM-2 model:

$$T=\Sigma T_ix_i+\Sigma\Sigma A_{ij}x_ix_j+\Sigma\Sigma B_{ij}x_ix_j(x_i-x_j)+\Sigma\Sigma C_{ij}x_ix_j(x_i-x_j)^2 \text{ (liquid phase)}$$
$$T=\Sigma T_iy_i+\Sigma\Sigma A'_{ij}y_iy_j+\Sigma\Sigma B'_{ij}y_iy_j(y_i-y_j)+\Sigma\Sigma C'_{ij}y_iy_j(y_i-y_j)^2 \text{ (vapor phase)} \tag{29}$$

where, A_{ij}, B_{ij} & C_{ij} are binary interaction parameters for liquid phase.

A'_{ij}, B'_{ij} & C'_{ij} are binary interaction parameters for vapor phase.

These two models, MRSM-1, and MRSM-2 model, have been compared and fitted with 26 group-group combinations of the possible 64 group-group combinations of whole organic compounds. The MRSM-2 model is found to be a slightly superior model to use for a general application. Nevertheless, MRSM-1 model can be used for various compounds of the less nonideality with slightly large variance of an estimation error.

Therefore, the generalized MRSM for N components is proposed as [Park et al., 1990; Park, 1992; Kim et al., 1995].

$$T=\sum_{i=1}^{N}T_ix_i+\sum\sum_{i\neq j}^{N-1\,N}A_{ij}x_ix_j+\sum\sum_{i\neq j}^{N-1\,N}B_{ij}x_ix_j(x_i-x_j)+\sum\sum_{i\neq j}^{N-1\,N}C_{ij}x_ix_j(x_i-x_j)^2 \text{ (liquid phase)}$$

$$T=\sum_{i=1}^{N}T_iy_i+\sum\sum_{i\neq j}^{N-1\,N}A'_{ij}y_iy_j+\sum\sum_{i\neq j}^{N-1\,N}B'_{ij}y_iy_j(y_i-y_j)+\sum\sum_{i\neq j}^{N-1\,N}C'_{ij}y_iy_j(y_i-y_j)^2 \text{ (vapor phase)} \tag{30}$$

When the MRSM is expanded to binary system;

$$T=T_1x_1+T_2x_2+A_{12}x_1x_2+B_{12}x_1x_2(x_1-x_2)+C_{12}x_1x_2(x_1-x_2)^2 \tag{31}$$

Similarly the MRSM can be expanded to ternary or quaternary. For ternary system:

$$\begin{aligned}T=&T_1x_1+T_2x_2+T_3x_3+A_{12}x_1x_2+A_{13}x_1x_3+A_{23}x_2x_3+B_{12}x_1x_2(x_1\\&-x_2)+B_{13}x_1x_3(x_1-x_3)+B_{23}x_2x_3(x_2-x_3)+C_{12}x_1x_2(x_1-x_2)^2\\&+C_{13}x_1x_3(x_1-x_3)^2+C_{23}x_2x_3(x_2-x_3)^2\end{aligned} \tag{32}$$

For quaternary system:

$$\begin{aligned}T=&T_1x_1+T_2x_2+T_3x_3+T_4x_4+A_{12}x_1x_2+A_{13}x_1x_3+A_{14}x_1x_4+A_{23}x_2x_3\\&+A_{24}x_2x_4+A_{34}x_3x_4+B_{12}x_1x_2(x_1-x_2)+B_{13}x_1x_3(x_1-x_3)\\&+B_{14}x_1x_4(x_1-x_4)+B_{23}x_2x_3(x_2-x_3)+B_{24}x_2x_4(x_2-x_4)+B_{34}x_3x_4\\&(x_3-x_4)+C_{12}x_1x_2(x_1-x_2)^2+C_{13}x_1x_3(x_1-x_3)^2+C_{14}x_1x_4(x_1-x_4)^2\\&+C_{23}x_2x_3(x_2-x_3)^2+C_{24}x_2x_4(x_2-x_4)^2+C_{34}x_3x_4(x_3-x_4)^2\end{aligned} \tag{33}$$

Then, the MRSM is transformed into the RSM model by replacing $x_3=1-x_1-x_2$, $x_3^2=(1-x_1-x_2)^2$, and $x_3^3=(1-x_1-x_2)^3$ or $x_4=1-x_1-x_2-x_3\cdots$ and so on with the regular requirement of $\Sigma x_i=1$ for liquid phase, $\Sigma y_i=1$ for vapor phase.

The RSM model requires estimation of the numerous unknown parameters for Eq. (27). To the contrary the MRSM-1 and MRSM-2 models contain only two and three unknown parameters [refer to Eq. (28) for MRSM-1 model and Eq. (29) for MRSM-2 model respectively] which can be estimated without experimental data.

RSM used as a statistical method of optimization will give maximum or minimum point on response surface. This concept is directly applied to engineering purpose to predict or estimate azeotropic point, maximum, minimum, saddle or cacoon on triangular plane for ternary system, tetrahedron corn for quaternary system.

THERMODYNAMIC EXPLANATION OF MRSM

From the fundamental relationship of thermodynamics, the general equation of Gibbs free energy is

$$d(nG)=(nV)dP-(nS)dT+\Sigma\mu_i dn_i \tag{34}$$

Eq. (34) may be written for each of liquid and vapor phases of the multicomponent system

$$d(nG)^{\alpha}=(nV)^{\alpha}dP-(nS)^{\alpha}dT+\Sigma\mu_i^{\alpha}dn_i \tag{35}$$

$$d(nG)^{\beta}=(nV)^{\beta}dP-(nS)^{\beta}dT+\Sigma\mu_i^{\beta}dn_i \tag{36}$$

At equilibrium

$$\Sigma\mu_i^{\alpha}dn_i+\Sigma\mu_i^{\beta}dn_i=0$$

therefore the total Gibbs free energy of the equilibrium system (closed) is expressed as;

$$dG=-SdT+VdP \tag{37}$$

For mixture, the Gibb's free energy change of the solution ΔG is

$$\Delta G=\Sigma x_i\cdot\Delta\overline{G}_i=\Sigma[x_i\{-S_i(\dot{T}_i-T^o)\}] \tag{38}$$

$$\begin{aligned}\Delta G^E&=\Delta G^{act}-\Delta G^{id}\\&=\Sigma[x_i\{-S_i^{act}(T^{act}-T^o)\}]-\Sigma[x_i\{-S_i^{id}(T^{id}-T^o)\}]\\&=\Sigma[x_i\{-(S_i^E+S_i-R\ln x_i)(T^{act}-T^o)\}]-\Sigma[x_i\{-(S_i-R\ln x_i)\\&\quad(T^{id}-T^o)\}]\\&=(-\Sigma x_iS_i+R\Sigma x_i\ln x_i)(T^{act}-T^{id})-\Sigma x_iS_i^E(T^{act}-T^o)\end{aligned} \tag{39}$$

The MRSM model is

$$T=\Sigma T_ix_i+\Sigma\Sigma A_{ij}x_ix_j+\Sigma\Sigma B_{ij}x_ix_j(x_i-x_j)+\Sigma\Sigma C_{ij}x_ix_j(x_i-x_j)^2 \tag{29}$$

Replacing the following with a reasonable assumption,

$$T=T^{act},\ T^{id}=\Sigma T_ix_i$$
$$T^{act}-T^{id}=\Sigma\Sigma A_{ij}x_ix_j+\Sigma\Sigma B_{ij}x_ix_j(x_i-x_j)+\Sigma\Sigma C_{ij}x_ix_j(x_i-x_j)^2 \tag{40}$$

Substituting Eq. (40) into Eq. (39), the following is obtained

$$\begin{aligned}\Delta G^E=&[(-\Sigma x_iS_i+R\Sigma x_i\ln x_i)\{\Sigma\Sigma A_{ij}x_ix_j+\Sigma\Sigma B_{ij}x_ix_j(x_i-x_j)\\&+\Sigma\Sigma C_{ij}x_ix_j(x_i-x_j)^2\}]-\Sigma[x_iS_i^E(T^{act}-T^o)]\end{aligned} \tag{41}$$

By definition of activity coefficient of the component i, γ_i can be given.

$$\begin{aligned}\ln\gamma_i&=\left[\frac{\partial(n\cdot\Delta G^E/RT)}{\partial n_i}\right]_{T,P,n_j}\\&=\frac{1}{RT}\left[\frac{\partial}{\partial n_i}[n\cdot[(-\Sigma x_iS_i+R\Sigma x_i\ln x_i)\cdot\{\Sigma\Sigma A_{ij}x_ix_j\right.\\&\quad+\Sigma\Sigma B_{ij}x_ix_j(x_i-x_j)+\Sigma\Sigma C_{ij}x_ix_j(x_i-x_j)^2-\Sigma x_iS_i^E(T_i^{act}\\&\quad\left.-T_i^o)\}]]\right]\end{aligned} \tag{42}$$

For multicomponent system, the activity coefficient of individual component i of the mixed solution can be expressed as a function of the MRSM model, such as shown by Eq. (42).

CONCLUSIONS

Recent advances and new developments in the field of molecular thermodynamics have made significant change on the concept of vapor liquid equilibrium. These advances necessitated introduction of the new concepts and methodologies.

MRSM is one of these new methodologies based on the theory of statistical and molecular thermodynamics. This was also found to be useful to engineers for predicting or seeking complex azeotropic mixture of ternary and quaternary systems. Further development of computer graphic simulation of this methodology is needed. Previous studies of the azeotropes for binary, ternary and quaternary systems had shown that a good agreement of the results between the experimental values of the published journals and the estimated values obtained by this methodology.

It is also possible to apply this technique for estimation of physical properties of liquid and gas phase mixtures.

ACKNOWLEDGEMENT

The authors wish to acknowledge the financial supports of ASAN Foundation (partial) and Kyung Hee University Research Fund of 1992 for this research project.

NOMENCLATURE

A_{12}, A_{13}, A_{14}, A_{23}, A_{24}, A_{34}, B_{12}, B_{13}, B_{14}, B_{23}, B_{24}, B_{34}, C_{12}, C_{13}, C_{14}, C_{23}, C_{24}, C_{34}: binary interaction parameters
A_{ij}, B_{ij}, C_{ij}, A'_{ij}, B'_{ij}, C'_{ij} : binary interaction parameters of component i & j defined by Eqs. (28), (29) & (30)
a, b, c, d, e, f, g, h, k, *l*, m, n, p, q, r : regression parameters of response surface model
b : parameter matrix
E(**b**) : expected value of unbiased estimation, **b**
E(**Y**) : expected value of unbiased estimation, **Y**
G : Gibbs free energy
G^E : excess Gibbs free energy
$g_i(r)$: pure pcf (pair correlation function)
g_{11}, g_{22}, g_{12}, g_{21}, g_{ij} : molecular interaction parameters or pair correlation function (pcf) due to the interaction force between two neighbour molecules
$g_{ij}(r)$: pcf of the mixed solution of i molecule and j molecule
N : number of data
n_i : number of moles of component i
N(L) : nearest-neighbour number
r : radius of sphere, position within molecule
r_{ij} : intermolecular distance
P : system pressure
R : gas constant
S : entropy
T : system temperature of mixture
T_i, T_j, T_1, T_2, T_3, T_4 : system temperature of pure component i, j, 1, 2, 3, 4
$\dot{T}$: $T=\Sigma x_iT_i+Tcorr=\Sigma x_i\dot{T}_i$
U_{ij} : pair potentials of molecule i and j
$W_{ij}(r)$: potential of mean force of molecule i and j
V : system volume
x_A, x_B: mixture composition
x_1, x_2,$\cdots$,x_i, x_j,$\cdots$, x_p : mole fraction of component 1, 2, $\cdots$, i, j, $\cdots$, p in liquid phase
X : variable vector, composition vector
Y : dependent variable vector
y_i, y_j, y_1, y_2, y_3, y_4 : mole fraction of component i, j, 1, 2, 3, 4 in vapor phase

$\mathbf{X}^T$: transpose of the matrix $\mathbf{X}$
$[\mathbf{X}^T\mathbf{X}]^{-1}$: inverse of matrix $[\mathbf{X}^T\mathbf{X}]$

Greek Letters

$\beta_1, \beta_2, \cdots, \beta_p$: expected value of parameter $b_1, b_2, \cdots, b_p$
$\boldsymbol{\beta}$: vector notation of parameter β
β : defined as $1/\kappa T$ of Eq. (1)
γ_i : activity coefficient of component i
ε_x : energy parameter of Eq. (2)
$\boldsymbol{\varepsilon}$: error vector
$\eta_1, \eta_2 \cdots, \eta_n$: expected value of dependent variable $Y_1, Y_2, \cdots, Y_n$
$\boldsymbol{\eta}$: vector notation of responses η
κ : proportionality constant
$\lambda, \lambda_{11}, \lambda_{22}, \lambda_{12}, \lambda_{21}$: molecular interaction parameters due to the interaction forces between two similar or different molecules in pure and mixed solution
Λ : Wilson's local composition parameter
ρ : density
σ : standard deviation of observation errors
σ_x : size parameter
$\boldsymbol{\Phi}$: covariance matrix of the observation errors
$\boldsymbol{\Omega}$: matrix of the known part of ϕ

Superscripts

E : excess property
act. : actual
id : ideal
0 : standard state

Subscripts

1,2,3,4$\cdots$: component 1, 2, 3, 4
A, B : molecules A & B
exp : exponential
i : component i
j : component j
i-j : i-j pair
pre. : predicted
o : pure
x : liquid composition

REFERENCES

Abram, D. S. and Prausnitz, J. M., "Statistical Thermodynamics of Liquid Mixtures: A New Expression for the Excess Gibbs Energy of Partly of Completely Miscible System", *AIChE J*, **21**, 116 (1975).

Box, G. E. P., "The Extrapolation and Exploitation of Response Surface: Some General Consideration and Examples", *Biometrics*, **10**, 16 (1954).

Chao, K. C. and Hougen, O. A., "Vapour-Liguid Equilibria in the Ternary System Ethyl Acetate-Benzene-Cyclohexane", *Chem. Eng. Sci.*, **7**, 246 (1958).

Fredenslund, A., Gmehling, J. and Rasmussen, P., "Vapor-Liquid Equilibrium Using UNIFAC", Elsevier, Amsterdam, 1979.

Gmehling, J., Onken, U. and Arlt, W., "Vapor-Liquid Equilibrium Data Collection", Chemistry Data Series, DECHEMA, Germany, 1981.

Ha, D. M. and Park, J. C., "The Representation of Ternary System by the Estimation of Group-Group and Interaction Parameters for MRSM-1 Model", *HWAHAK KONGHAK*, **29**(3), 284 (1991).

Hill, W. J. and Hunter, W. G., "A Review of Response Surface Methodology: A Literature Survey", *Technometric*, **8**, 571 (1966).

Hilm, A. K., Ellis, S. R. M. and Barker, P. E., "Method of Evaluating Activity Coefficient Parameters", *British Chemical Engineering*, **15**, 1321 (1970).

Hu, Y., Liu, H. and Prausnitz, J. M., "A Model-Free Method for Calculating Vapor-Liquid Equilibria for Multicomponent Systems from Total-Pressure of Boiling-Point Data", *Fluid Phase Equilibria*, **93**, 73 (1994).

Kim, M. G., Ha, D. M. and Park, J. C., "Modified Response Surface Methodology (MRSM) for Phase Equilibrium-Application", *KJChE*, **12**(1), 39 (1995).

King, M. B., "Phase Equilibrium in Mixtures", Pergamon Press, London, 1969.

Kojima, K. and Tochigi, K., "Prediction of Vapor-Liquid Equilibria by the ASOG Method", Elsevier, Amsterdam, 1979.

Lee, L. L. and Starling, K. E., "The Statistical Mechanical Local Composition Theory: The Balance Equations and Concentration Effects in Nonideal Mixtures", *Fluid Phase Equilibria*, **21**, 77 (1985).

Lee, L. L., "Molecular Thermodynamics of Nonideal Fluids", Butterworths, Boston, 1988.

Lu, B. C. Y., Li, J. C. M. and Ting, T. W., "Cluster Theory of Vapor-Liquid Equilibria", *Ind. Eng. Chem.*, **51**, 219 (1959).

Malesinski, W., "Azeotropy and Other Theoretical Problems of Vapor-Liquid Equilibrium", Polish Scientific Publishers, Warszawa, 1965.

Nagata, I., "Vapor-Liquid Equilibria for the Ternary System Methyl Acetate-Benzene-Cyclohexane", *J. Chem, Eng. Data*, **7**, 461 (1962).

Park, J. C., "Prediction of the Activity Coefficients for Non-Ideal Liquid Mixtures", The 183rd Meeting of European Federation of Chem. Engineers at Helsinki, Finland, June (1977).

Park, J. C., "Estimation of the Activity Coefficients for Non-Ideal Liquid Mixtures", Theses Collection, Kyung Hee Univ., **9**, 555 (1979).

Park, J. C., "Estimation of the Activity Coefficients for Non-Ideal Liquid Mixtures: Effect of Variables of TPTT Equations on Response Model of Molecular Interaction Energy Parameters of Two and Three Component Systems", Theses Collection, Kyung Hee Univ., **11**, 139 (1982).

Park, J. C., "Estimation of Activity Coefficients for Non-Ideal Liquid Mixtures: Selection of Response Surface Model by Means of Response Surface Methodology for Multicomponent System", PACHEC Proceeding, **2**, 340 (1983).

Park, J. C., "Estimation of Multicomponent Phase Surface by Means of Response Surface Methodology and Comparison of Fitting for 3 & 4 Component Systems", Kyung Hee Univ. Publication, Seoul, Korea, 1985.

Park, J. C., "The Partial Molar Interaction Energy of the TPTT Equation", Theses Collection, Kyung Hee Univ., **15**, 239 (1986).

Park, J. C., "Representation of Multiple Phase Response Surface by Means of Computer Graphics", Kyung Hee Univ. Publication, Seoul, Korea, 1987.

Park, J. C. and Kim, M. G., "Comparative Analysis of the TPTT, MPMT and RSM Models", *HWAHAK KONGHAK*, **26**(2), 194 (1988).

Park, J. C., "Mandang, Park, Jong-Chul, Ph.D., Full Professor, 60th Birthday Anniversary Theses Collection", Munyangsa, Seoul, Korea, 1988.

Park, J. C., Ha, D. M. and Kim, M. G., "Estimation Methodology of Multicomponent Phase Equilibria by Group-Group and Interaction Parameters", Proc. 5th APCChE Congress, 4a-14, Kuala Lumpur, Malaysia (1990).

Park, J. C., "Theory and Practice of Modified Response Surface Methodology in Phase Equilibrium", KIChE meeting, April (1991a).

Park, J. C., "Theory and Practice of Modified Response Surface Methodology in Phase Equilibrium", 68th Annual Meeting of the Korean Chemical Society, Changwon, Korea (1991b).

Park, J. C., "Mandang, Park, Jong Chul, Ph.D. Honorable Retirement Commemoration Theses Collection", Munyangsa, Seoul, Korea, 1992.

Prausnitz, J. M., Lichtenthaler, R. N. and de Azevedo, E. G., "Molecular Thermodynamics of Fluid Phase Equilibria", 2nd ed., Prentice-Hall Inc. Englewood Cliffs, N.J., 1986.

Redlich, O. and Kister, A. T., "On the Thermodynamics of Non-Electrolyte Solution and Its Technical Application: III. Systems with Associated Components", *J. Chem. Phys.*, **15**, 849 (1947).

Reid, R. C., Prausnitz, J. M. and Poling, P. E., "The Properties of Gases and Liquids", 3rd ed., McGraw-Hill, New York, 1986.

Renon, H. and Prausnitz, J. M., "Local Compositions in Thermodynamic Excess Functions for Liquid Mixtures", *AIChE J.*, **14**, 135 (1968).

Shin, H. S. and Park, J. C., "Comparison of Methods of Estimating VLE by Means of the Wilson, NRTL, UNIQUAC Equations for Ternary Systems by Computer Graphics", Theses Collection, Kyung Hee Univ., **17**, 497 (1988).

Wilson, G. M., "Vapor-Liquid Equilibrium. XI. A New Expression for the Excess Energy of Mixing", *J. Am. Chem. Soc.*, **86**, 127 (1964).

Wisniak, J. and Tamir, A., "Vapor-Liquid Equilibria in the Ternary Systems Water-Formic Acid-Acetic Acid and Water-Acetic Acid-Propionic Acid", *J. Chem. Eng. Data*, **22**, 253 (1977).