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MODIFIED RESPONSE SURFACE METHODOLOGY (MRSM) FOR PHASE EQUILIBRIUM-APPLICATION

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Abstract—Attempts are being made to predict multicomponent azeotropic mixtures from the physical property of pure component and compositions of the constituting binary combination pairs. A modified response surface methodology (MRSM) model has been proposed which correlates boiling temperatures of binary, ternary and quaternary mixtures directly with the compositions of vapor and liquid phases. The generalized MRSM-2 models for liquid and vapor phases are proposed as follows:

$$T=\sum_{i=1}^{N} T_iX_i+\sum_{i\neq j}^{N-1N}\sum A_{ij}\ X_iX_j+\sum_{i\neq j}^{N-1N}\sum B_{ij}\ X_iX_j(X_i-X_j)+\sum_{i\neq j}^{N-1N}\sum C_{ij}\ X_iX_j(X_i-X_j)^2 \quad \text{(for liquid phase)}$$

$$T=\sum_{i=1}^{N} T_iY_i+\sum_{i\neq j}^{N-1N}\sum A_{ij}\ Y_iY_j+\sum_{i\neq j}^{N-1N}\sum B_{ij}\ Y_iY_j(Y_i-Y_j)+\sum_{i\neq j}^{N-1N}\sum C_{ij}\ Y_iY_j(Y_i-Y_j)^2 \quad \text{(for vapor phase)}$$

These models require normal boiling point of the pure components, T_i and group-group parameters A_{ij}, B_{ij} & C_{ij} which can be estimated by the group-group concepts of the constituent components. Therefore, this methodology is applied for the system of three and four components by the computer simulation. No experimental data is required for seeking of composition and temperature of the multicomponent azeotropic mixtures. By means of this methodology, MRSM, it is possible to depict an isothermal line map, temperature contours of the individual phase of the constituting ternaries for each quaternary system. Furthermore, it is possible to predict the azeotropic behaviors, maximum, minimum, saddle or any other type of azeotropic mixtures by examining the graphic contours obtained by computer graphics in the triangular coordinate for ternary and tetrahedron for quaternary. The proposed methodology (MRSM model) has been tested and compared successfully with previously reported azeotropic data in various journals for several ternary and quaternary multicomponent systems. Two azeotropic mixtures are newly found for each of two different quaternary tetrahedrons. The composition, temperature and type of the newly found azeotropes are reported.

Keywords: *Group-group Parameter, Interaction Parameter, Modified Response Surface Methodology (MRSM), Quaternary Azeotropic Mixture, Two Parameters and Two Terms (TPTT) Equations*

INTRODUCTION

The proposed MRSM-2 model is able to correlate directly the relationship between the boiling temperatures at binary, ternary and quaternary systems and the compositions of vapor and liquid phases in equilibrium. Also, this methodology should provide an information about the solution azeotrope (type, temperature & composition) without experimental data in ternary & quaternary systems by means of the proposed MRSM-2.

Since no adequate method is currently available for the quaternary systems, this simulation method demonstrated a possibility of predicting these complex azeotropic behaviors of quaternary system which is rather difficult to seek even by the sophisticated experimental method.

Futhermore, this methodology shows the possibility of estimation not only the azeotropic behavior but also the properties of various fluids.

MODIFIED RESPONSE SURFACE METHODOLOGY FOR TERNARY AND QUATERNARY

1. Quaternary Systems Selected

In order to investigate adaptability of MRSM methodology for ternary and quaternary systems, the following three quaternary systems have been selected [1-8, 16]. Since these systems have been previously published in the well-accepted journals [1-3], accuracy of experimental work is reasonably reliable.

Also, entire ternary and binary systems of each constituting components of the quaternaries are available in the published journals [1-3] [exception of two ternary systems: MEK(1)-cyclohexane(3)-2-propanol(4) and methyl acetate(1)-methanol(3)-benzene(4)].

System I : Methyl ethyl ketone(1)-Benzene(2)-Cyclohexane(3)-2-Propanol(4) Constituting ternary systems
1. Methyl ethyl ketone(1)-Benzene(2)-Cyclohexane(3)
2. Methyl ethyl ketone(1)-Benzene(2)-2-Propanol(4)
3. Methyl ethyl ketone(1)-Cyclohexane(3)-2-Propanol(4)
4. Benzene(2)-Cyclohexane(3)-2-Propanol(4)

System II : Water(1)-Formic acid(2)-Acetic acid(3)-Propionic acid (4) Constituting ternary systems
1. Water(1)-Formic acid(2)-Acetic acid(3)
2. Water(1)-Formic acid(2)-Propionic acid(4)

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3. Water(1)-Acetic acid(3)-Propionic acid(4)
4. Formic acid(2)-Acetic acid(3)-Propionic acid(4)

System III : Methyl acetate(1)-Chloroform(2)-Methanol(3)-Benzene(4) Constituting ternary systems

1. Methyl acetate(1)-Chloroform(2)-Methanol(3)
2. Methyl acetate(1)-Chloroform(2)-Benzene(4)
3. Methyl acetate(1)-Methanol(3)-Benzene(4)
4. Chloroform(2)-Methanol(3)-Benzene(4)

2. Binary Interaction Parameters

In order to estimate the phase temperature T from phase composition x_1, x_2,$\cdots$ for the multicomponent system by means of the generalized MRSM equation the binary interaction parameters A_{ij}, B_{ij}, C_{ij} have to be known [7-11].

A slight modification of the previously suggested estimation method of the critical temperature of mixtures was utilized for this purpose [12].

The suggested equations to estimate the interaction parameters A_{ij}, B_{ij}, and C_{ij} are as follows;

$$A_{ij}=(1/2)\phi_T^A(T_i+T_j) \quad (1)$$

$$B_{ij}=(1/2)\phi_T^B(T_i+T_j) \quad (2)$$

$$C_{ij}=(1/2)\phi_T^C(T_i+T_j) \quad (3)$$

ϕ_T^A, ϕ_T^B, ϕ_T^C of the above equations are also estimated by Eqs. (4)-(6) [7-11].

$$\phi_T^A=\alpha+(\beta/\theta_T)+\gamma(\ln\theta_T)+\delta\theta_T+\varepsilon\theta_T^2+\eta\theta_T^3 \quad (4)$$

$$\phi_T^B=\alpha'+(\beta'/\theta_T)+\gamma'(\ln\theta_T)+\delta'\theta_T+\varepsilon'\theta_T^2+\eta'\theta_T^3 \quad (5)$$

$$\phi_T^C=\alpha''+(\beta''/\theta_T)+\gamma''(\ln\theta_T)+\delta''\theta_T+\varepsilon''\theta_T^2+\eta''\theta_T^3 \quad (6)$$

θ_T of the Eqs. (4)-(6) is calculated from the normal boiling points of components i and j of the selected group-group.

$$\theta_T=\left|\frac{T_i-T_j}{T_i+T_j}\right| \quad (7)$$

where α, β, γ, δ, ε, η,
α', β', γ', δ', ε', η',
α'', β'', γ'', δ'', ε'', η'' are the group-group parameters.

3. Group-Group Parameters

Estimation of the binary interaction parameters A_{ij}, B_{ij}, C_{ij} from Eqs. (1)-(3) & (4)-(6) and (7) require the values of six group-group parameters for each interaction parameters [7-11, 16-18].

A_{ij} : α, β, γ, δ, ε, η
B_{ij} : α', β', γ', δ', ε', η',
C_{ij} : α'', β'', γ'', δ'', ε'', η''

This method, which has been established to predict the temperature of mixtures, is not limited to specific mixtures but intended to apply to the whole non-electrolytes except electrolytes and polymer solutions.

For this purpose, organic compounds of the selected three quaternary systems for this study are classified into eight chemical functional groups; paraffin, aromatic, alcohol, halogen, ester, ketone, acid, and water. By combining these eight chemical functional groups for binary group-group; thirteen binary group-groups were obtained, as shown on Table 1.

In order to obtain a reliable value of each individual group-group parameters 100 experimental data sets (1958 data points) of vapor liquid equilibrium of the binary systems previously published and collected on the references were utilized [1-3].

Table 1. Number of data points and data sets for the selected binary group-group systems [1-3]

Group-group systems	No. of data sets	No. of points	Group-group systems	No. of data sets	No. of points
Aromatic-Paraffin	11	259	Alcohol-Ester	8	126
Alcohol-Paraffin	9	164	Ketone-Paraffin	6	82
Alcohol-Aromatic	8	207	Alcohol-Ketone	11	182
Aromatic-Halogen	7	148	Acid-Water	5	122
Aromatic-Ester	7	126	Acid-Acid	6	102
Alcohol-Halogen	9	165	Aromatic-Ketone	6	122
Ester-Halogen	7	153			
			Total	100	1958

Table 2. The binary group-group parameters of aromatic-paraffin system for calculating binary interaction parameter

	Liquid phase					
	A_{12}		B_{12}		C_{12}	
Aromatic -Paraffin	α	0.468280	α'	1.733502	α''	−3.189149
	β	0.000157	β'	0.000489	β''	−0.000952
	γ	0.096055	γ'	0.322962	γ''	−0.601712
	δ	−9.227683	δ'	−34.599942	δ''	60.895388
	ε	139.845901	ε'	596.875557	ε''	−992.435205
	η	−1175.835696	η'	−3943.541078	η''	6512.989281
	Vapor phase					
	A_{12}		B_{12}		C_{12}	
	α	−1.884406	α'	0.635579	α''	0.365289
	β	−0.000530	β'	0.000168	β''	0.000063
	γ	−0.345598	γ'	0.116650	γ''	0.059826
	δ	37.569492	δ'	−14.886959	δ''	−10.645614
	ε	−608.237086	ε'	279.500767	ε''	206.924048
	η	4244.155933	η'	−1950.782501	η''	−1457.255270

For individual group-group parameter, several reliable data sets are selected from the above reference, then the parameters are estimated by a multiple regression for liquid and vapor phases [4, 13-15].

As an example of aromatic-paraffin system, 259 data points of the 11 sets were utilized for this computation. For each selected binary group-group system, a summary of number of data sets and number of points utilized for each computation are summarized in Table 1.

Table 2 shows the results of the six computed values, binary group-group parameters, α, β, γ, δ, ε, η for each three binary interaction parameters A_{ij}, B_{ij}, C_{ij} for liquid and vapor phases of the aromatic-paraffin system (the rest of 12 of 13 systems are shown on the Appendix) [7-9, 17].

REPRESENTATION OF ISOTHERMAL LINES BY COMPUTER GRAPHICS

1. Temperature Contour Map, Triangular and Tetrahedron

VLE behavior of the binary systems can be understood from the correlation between temperature and composition. However phenomena of phase surface is not able to be observed and visualized accurately for ternary and quaternary systems by vapor-

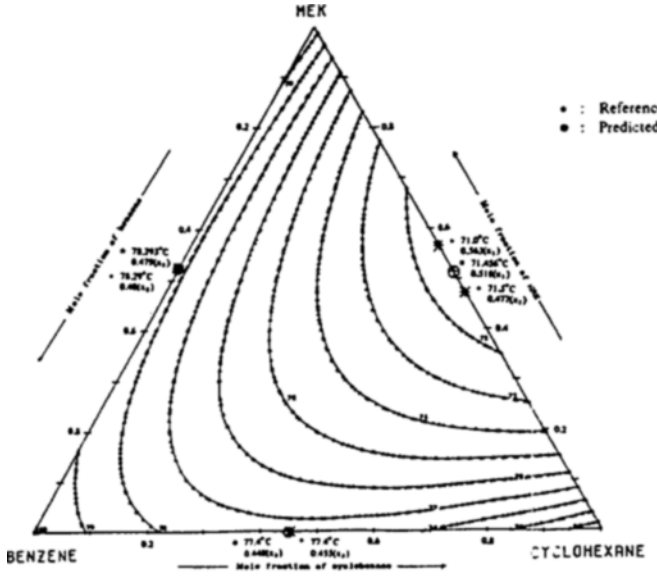

Fig. 1. Isothermal line of MEK-benzene-cyclohexane system predicted by MRSM-2 model (liquid phase).

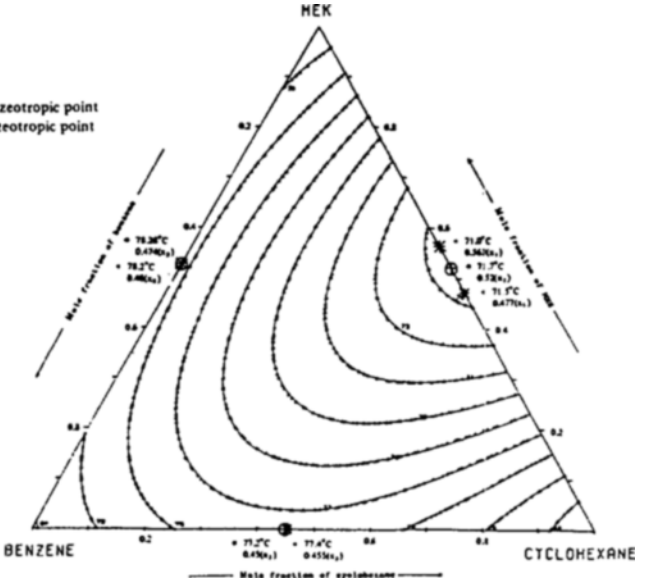

Fig. 2. Isothermal line of MEK-benzene-cyclohexane system predicted by MRSM-2 model (vapor phase).

liquid equilibrium data alone. Especially, in the case of azeotropic mixtures of saddle or any other complex type, prediction of azeotropic point, temperature and composition, is rather difficult even by experimental work. It has been known that the discrepancy among the reported values of the literatures was not rare [1-3].

This approach is to show that visual analysis is feasible by plotting isothermal lines of phase surface of ternary and quaternary systems using MRSM model and to predict existence of azeotropes, type, composition and temperature. Furthermore, the phenomena of multicomponent vapor-liquid equilibrium phase surface can be studied by examining shifting locus of azeotropic point, observation of temperature distribution and composition of the phase surface [5-11, 16-18].

For ternary system, the temperature contours with change of composition of the liquid and vapor phases can be represented on a plane (isotherm map). However isotherms of quaternary system can be depicted stereographically only in three-dimensional space. Therefore geometry of tetrahedron has been adapted to depict isotherms stereographically in three-dimensional space so that the sum of each composition is unit at any arbitrary point. Isothermal lines are illustrated in Fig. 1 & 2, which is one of four ternaries of vapor and liquid phases* of the selected quaternary systems MEK(1)-benzene(2)-cyclohexane(3)-2-propanol(4) [8, 9, 16, 18].

Each phase of four tetrahedron and 20, 40, 60 and 80% planes** (Fig. 3) of the top components x_4, and y_4 are drawn individually by the computer graphics. Then, these eight planes are reassembled to construct one of each tetrahedron corn for liquid and vapor phases [7-9].

Each phase of three tetrahedron except for the bottom-facets are shown by rotating 120° as for the liquid phase (Fig. 4) and vapor phase (Fig. 5).

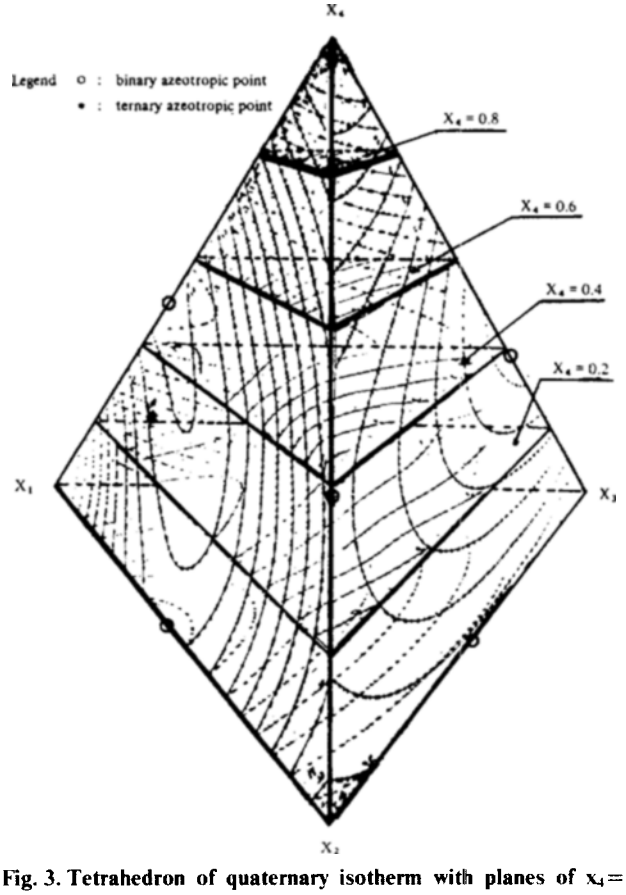

Fig. 3. Tetrahedron of quaternary isotherm with planes of $x_4=0$, 0.2, 0.4, 0.6 and 0.8 mole fractions.

It has been observed that individual isothermal line of each phase is precisely matched at every point of phase intersection.

2. Algorithms of the Isotherm Map

In order to plot the isothermal lines by computer graphics, two steps are required. That is, computing various compositions for

*Other six ternary isotherm maps of three vapor and three liqulid phases can be obtained from the author by request.

**Ternary isotherm maps can be obtained from the author by request.

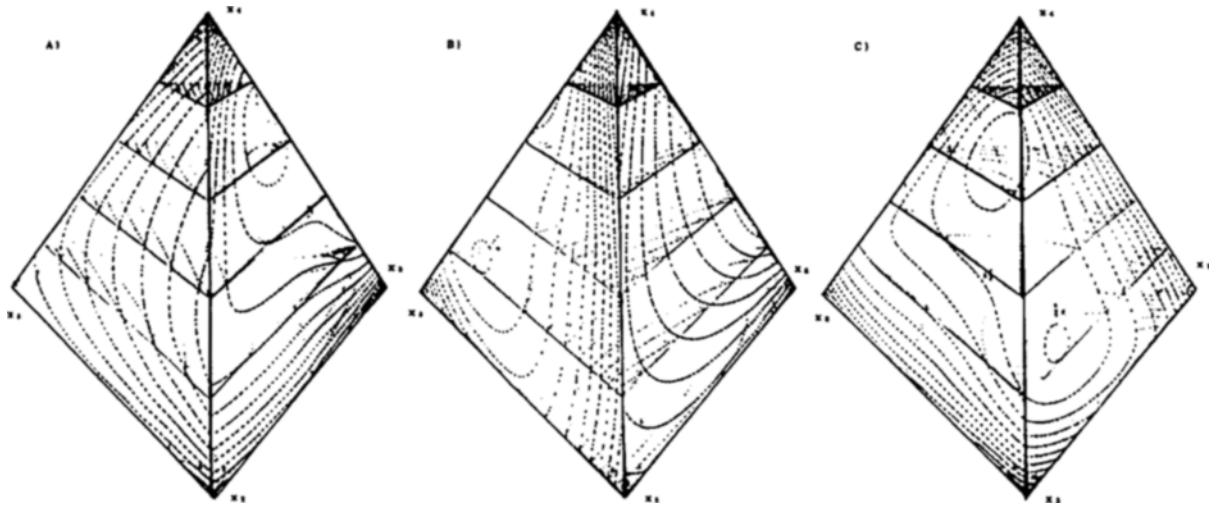

Fig. 4. Isothermal lines of quaternary tetrahedron, system MEK(1)-benzene(2)-cyclohexane(3)-2-propanol(4). At three different angle of views (liquid phase).

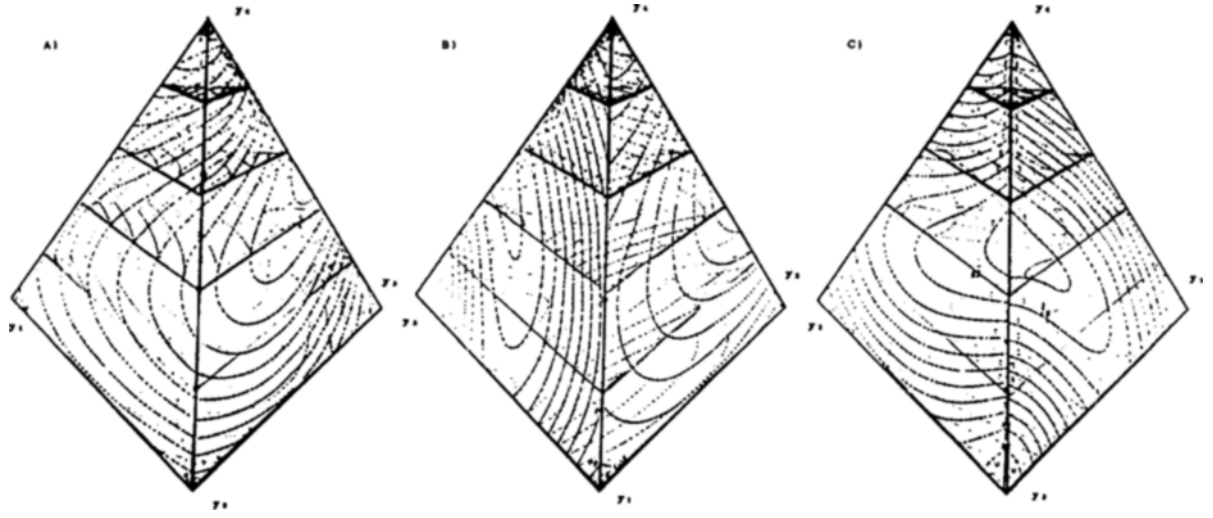

Fig. 5. Isothermal lines of quaternary tetrahedron system MEK(1)-benzene(2)-cyclohexane(3)-2-propanol(4). At three different angle of views (vapor phase).

given isotherm temperature and then plotting isothermal lines on paper on triangular coordinates. The Newton-Raphson algorithm with the formula of MRSM is utilized for the first step and coordination algorithm XX, YY with a size factor α of plotting isotherms on triangular coordinate for the second step.

1st step:

Ternary system isotherm

$$x_{n+1} = x_n - FT(x_i)/FT'(x_i) \tag{8}$$

$$FT(x_i) = \sum_{i=1}^{3} T_i x_i + \sum_{i}^{2}\sum_{j}^{3} A_{ij} x_i x_j + \sum_{i}^{2}\sum_{j}^{3} B_{ij} x_i x_j (x_i - x_j) + \sum_{i}^{2}\sum_{j}^{3} C_{ij} x_i x_j (x_i - x_j)^2 - T = 0 \tag{9}$$

Quaternary system isotherm

$$x_{n+1} = x_n - FT(x_i)/FT'(x_i) \tag{10}$$

$$FT(x_i) = \sum_{i=1}^{4} T_i x_i + \sum_{i}^{3}\sum_{j}^{4} A_{ij} x_i x_j + \sum_{i}^{3}\sum_{j}^{4} B_{ij} x_i x_j (x_i - x_j) + \sum_{i}^{3}\sum_{j}^{4} C_{ij} x_i x_j (x_i - x_j)^2 - T = 0 \tag{11}$$

Whereas, $FT(x_i)$ is the difference between the estimated temperature of the mixture T by the MRSM formula and the given temperature T of the isotherm.

$FT'(x_i)$ is a formula obtained from partial differentiation of FT (x_i) with respect to composition x_i. For ternary, $\Sigma x_i = 1$ also $x_2 = 1 - x_1 - x_3$, then fixing temperature T and one of the composition x_1, one of the rest composition x_2 or x_3 is varied with a fixed internal (such as 0.02) for the Newton-Raphson computation. When absolute value of $FT(x_i)$ has been obtained within the range of allowable error (such as 0.0001), the computed compositions can be accepted.

Subsequently, similar computation is repeated for the other composition. Then the third composition is computed from the predetermined first and second compositions. This composition is accepted as an equilibrium composition at the given temperature T. For quaternary, the similar computations are repeated for indivi-

Table 3. Summary of mean A.P.E. of liquid and vapor phases for thirteen binary group-group, constituting three quaternary systems

Group-Group systems	Mean A.P.E.	
	Liquid	Vapor
Aromatic-Paraffin	0.2960	0.3504
Alcohol-Paraffin	1.6673	1.6415
Alcohol-Aromatic	1.0902	1.0635
Aromatic-Halogen	0.1926	0.2346
Aromatic-Ester	0.8554	0.8535
Alcohol-Halogen	1.5602	1.3060
Ester-Halogen	1.3349	1.3071
Alcohol-Ester	0.4156	0.3703
Ketone-Paraffin	0.7379	0.6771
Alcohol-Ketone	1.0456	0.9944
Acid-Water	0.4259	0.4494
Acid-Acid	0.3531	0.3797
Aromatic-Ketone	0.3341	0.4004
Total mean A.P.E.	0.7930	0.7714

dual four triangular surfaces; after fixing the composition of x_4 with an incremental interval of 0.2, 0.4, 0.6, 0.8, the isotherm composition of four intermediate triangular surfaces are also computed with the similar method [7, 8, 16].

2nd step: The computed compositions x_1, x_2, x_3 and x_4 are plotted on the triangular coordinate. The algorithm used for this purpose is:

$$XX=[x_1\cos(\pi/3)+x_3]\alpha \tag{12}$$

$$YY=[x_1\sin(\pi/3)]\alpha \tag{13}$$

Whereas, α is size factor of the triangle. XX and YY are the coordinate number on the rectangular coordinate after transforming individual compositions, therefore the isothermal line is obtained by connecting respective coordinate values of XX, YY for a given temperature [7, 8, 16].

TEST RESULTS AND COMPARATIVE ANALYSIS

1. Comparison of Phase Temperature

In order to evaluate a feasibility or goodness of the modified Response Surface Methodology for estimation of multicomponent vapor and liquid equilibrium temperatures and to predict a type, location and composition of various azeotropic mixtures, the previously reported experimental data on journals [1-3] and the estimated data by the MRSM were compared for binary, ternary and quaternary systems [7, 8, 16]. Average percentage error between two values are calculated and listed in Table 3 for binary, Table 4 for ternary and Table 5 for quaternary.

$$A.P.E.=\frac{\sum_{i}^{n}|T_{prc}-T_{exp}|/T_{exp}}{N}\times 100 \tag{14}$$

For thirteen binary group-group systems of this study constituting binary group-group systems of three quaternaries, the mean APE was 0.79 for liquid phase and 0.77 for vapor phase. Similarly, for ten ternary systems, the mean APE was 1.25 for liquid phase and 1.22 for vapor phase. Among these ten ternary systems, a system of chloroform-methanol-benzene showed an exceptionally high value 4.298 for liquid and 3.484 for vapor phases, which compare with the rest of the nine systems whose average value is 0.910 for liquid and 0.969 for vapor phases. A reason of high APE for chloroform-methanol-benzene system could be caused with a large deviation of experimental data of this particular system. The simulated results are in good agreement with experimental data previously published on the various journals within the statistically reasonable experimental errors.

Table 4. Summary of mean A.P.E. of liquid and vapor phases for ten ternaries constituting three quaternary systems

Systems	Phase	A.P.E.
MEK(1)-benzene(2)-cyclohexane(3)	Liquid	0.52
	Vapor	0.54
MEK(1)-benzene(2)-2-propanol(4)	Liquid	0.31
	Vapor	0.41
Benzene(2)-cyclohexane(3)-2-propanol(4)	Liquid	1.57
	Vapor	1.12
Water(1)-formic acid(2)-acetic acid(3)	Liquid	1.28
	Vapor	0.78
Water(1)-formic acid(2)-prop. acid(4)	Liquid	1.45
	Vapor	1.40
Water(1)-acetic acid(3)-prop. acid(4)	Liquid	0.78
	Vapor	1.16
Formic acid(2)-acetic acid(3)-prop. acid(4)	Liquid	0.64
	Vapor	0.58
Methyl acetate(1)-chloroform(2)-methanol(3)	Liquid	1.11
	Vapor	1.15
Methyl acetate(1)-chloroform(2)-benzene(4)	Liquid	0.54
	Vapor	1.60
Chloroform(2)-methanol(3)-benzene(4)	Liquid	4.30
	Vapor	3.48

Table 5. Summary of mean A.P.E. of liquid and vapor phases for three quaternary systems

	I		II		III	
Systems	MEK(1)-Benzene(2)-Cyclohexane(3)-2-Propanol(4)		Water(1)-Formic acid(2)-Acetic acid(3)-Propionic acid(4)		Methyl acetate(1)-Chloroform(2)-Methanol(3)-Benzene(4)	
Phase	Liquid	Vapor	Liquid	Vapor	Liquid	Vapor
mean A.P.E.	0.69	0.94	0.55	2.01	2.80	2.92

For three quaternary systems, liquid and vapor phases of system I and liquid phase of system II show APE less than 1.0%, ranging 0.94-0.64, while vapor phase of system II, liquid and vapor phases of system III show about 2.0-2.92%.

2. Azeotropes

Comparison between the reported and graphically predicted values of azeotropic mixture at 760mmHg for three quaternaries, and subsequently constituting ternaries and binaries are listed in Table 6, 7 and 8.

In general, types of the azeotropic mixture; maximum, minimum or saddle types agree well with previously reported types of binaries and ternaries. However, temperatures and compositions of azeotropic points showed a slight difference for some cases.

Particular importance of this study is that the special type of azeotropic mixtures for quaternary system are newly found for system I, MEK(1)-benzene(2)-cyclohexane(3)-2-propanol(4) and

Table 6. Comparison between the reported data and graphically predicted values of the azeotropic point at 760 mmHg for system I, MEK(1)-benzene(2)-cyclohexane(3)-2-propanol(4), based on MRSM

(1) Quaternary system

Systems	Components	Reported data mole	T, ℃	MRSM-2 model Liquid mole	T, ℃	Vapor mole	T, ℃	Type of azeotrope
I	MEK(1)	none		0.009	69.77	0.009	69.77	cocoon
	Benzene(2)			0.012		0.012		
	Cyclohexane(3)			0.529		0.529		
	2-Propanol(4)			0.450		0.450		

(2) Ternary systems

Systems	Components	Reported data mole	T, ℃	MRSM-2 model Liquid mole	T, ℃	Vapor mole	T, ℃	Type of azeotrope
I-3-1	MEK(1)	none		none				
	Benzene(2)							
	Cyclohexane(3)							
I-3-2	MEK(1)	none		none				
	Benzene(2)							
	2-Propanol(4)							
I-3-3	MEK(1)	0.174	68.9	0.140	68.9	uncertain		min.
	Cyclohexane(3)	0.535		0.620				
	2-Propanol(4)	0.291		0.240				
I-3-4	Benzene(2)	0.142	69.1	0.100	68.5	uncertain		min.
	Cyclohexane(3)	0.474		0.260				
	2-Propanol(4)	0.384		0.640				

(3) Binary systems

Systems	Components	Reported data mole	T, ℃	MRSM-2 model Liquid mole	T, ℃	Vapor mole	T, ℃	Type of azeotrope
I-2-1	MEK(1)	0.520	78.29	0.521	78.29	0.526	78.28	min.
	Benzene(2)	0.480		0.479		0.474		
I-2-2	MEK(1)	0.477	71.5	0.516	71.46	0.520	71.7	min.
	Cyclohexane(3)	0.523		0.484		0.480		
I-2-3	MEK(1)	0.618	77.7	0.616	77.35	0.643	77.2	min.
	2-Propanol(4)	0.382		0.384		0.357		
I-2-4	Benzene(2)	0.545	77.4	0.552	77.4	0.550	77.2	min.
	Cyclohexane(3)	0.455		0.448		0.450		
I-2-5	Benzene(2)	0.605	71.92	0.681	71.5	0.600	72.5	min.
	2-Propanol(4)	0.395		0.319		0.400		
I-2-6	Cyclohexane(3)	0.595	69.6	0.282	68.72	0.500	69.5	min.
	2-Propanol(4)	0.405		0.718		0.500		

mole: mole fraction, T: temperature, min.: minimum azeotrope

Table 7. Comparison between the reported data and graphically predicted values of the azeotropic point at 760 mmHg for system II, water(1)-formic acid(2)-acetic acid(3)-propionic acid(4), based on MRSM

(1) Quaternary system

Systems	Components	Reported data mole	T, ℃	MRSM-2 model Liquid mole	T, ℃	Vapor mole	T, ℃	Type of azeotrope
II	Water(1)	none		0.309	106.3	0.360	107.7	saddle
	Formic acid(2)			0.426		0.494		
	Acetic acid(3)			0.245		0.126		
	Prop. acid(4)			0.020		0.020		

(2) Ternary systems

Systems	Components	Reported data mole	T, ℃	MRSM-2 model Liquid mole	T, ℃	Vapor mole	T, ℃	Type of azeotrope
II-3-1	Water(1)	0.363	107.0	0.300	106.3	0.370	107.2	saddle
	Formic acid(2)	0.469		0.430		0.480		
	Acetic acid(3)	0.168		0.270		0.150		
II-3-2	Water(1)	0.420	107.5	0.350	107.1	0.427	107.4	saddle
	Formic acid(2)	0.540		0.540		0.563		
	Prop. acid(4)	0.040		0.110		0.010		
II-3-3	Water(1)	none		none				
	Acetic acid(3)							
	Prop. acid(4)							
II-3-4	Formic acid(2)	none		none				
	Acetic acid(3)							
	Prop. acid(4)							

(3) Binary systems

Systems	Components	Reported data mole	T, ℃	MRSM-2 model Liquid mole	T, ℃	Vapor mole	T, ℃	Type of azeotrope
II-2-1	Water(1)	0.424	107.6	0.421	107.52	0.388	107.61	min.
	Formic acid(2)	0.576		0.579		0.612		
II-2-2	Water(1)	none		none				
	Acetic acid(3)							
II-2-3	Water(1)	0.950	99.8	0.934	99.58	0.987	99.96	min.
	Prop. acid(4)	0.050		0.066		0.013		
II-2-4	Formic acid(2)	none		none				
	Acetic acid(3)							
II-2-5	Formic acid(2)	none		none				
	Prop. acid(4)							
II-2-6	Acetic acid(2)	none		none				
	Prop. acid(4)							

system II, water(1)-formic acid(2)-acetic acid(3)-propionic acid(4) (refer to Table 6, 7 & 8). These quaternary azeotropes are not reported or appeared on any reference previously. A cocoon type isotherm contour in the tetrahedron of system I is a particularly worthy phenomena to mention [8, 9, 18].

CONCLUSIONS

1. Due to various assumptions and simplifications associated with TPTT and MPMT equations, the MRSM model was proposed as one of the new methods of estimating temperatures of phase equilibrium systems.

2. Majority of estimating methods for phase equilibrium compositions is to predict activity coefficient first; subseqently, equilibrium phase composition was estimated. However, a newly proposed method, MRSM model, makes it possible to estimate phase temperature and vapor phase composition directly from a given liquid phase composition without any experimental work or data.

3. MRSM model, similar to the TCR equation, which is useful for practical engineering has been proposed, and a generalized form for N-component system is as follows:

Table 8. Comparison between the reported data and graphically predicted values of the azeotropic point at 760 mmHg for system III, methyl acetate(1)-chloroform(2)-methanol(3)-benzene(4), based on MRSM

(1) Quaternary system

Systems	Components	Reported data mole	Reported data T, ℃	MRSM-2 model Liquid mole	MRSM-2 model Liquid T, ℃	MRSM-2 model Vapor mole	MRSM-2 model Vapor T, ℃	Type of azeotrope
III	Methyl acetate(1) Chloroform(2) Methanol(3) Benzene(4)	none		none				

(2) Ternary systems

Systems	Components	Reported data mole	Reported data T, ℃	MRSM-2 model Liquid mole	MRSM-2 model Liquid T, ℃	MRSM-2 model Vapor mole	MRSM-2 model Vapor T, ℃	Type of azeotrope
III-3-1	Methyl acetate(1)	0.263	56.4	0.260	55.7	0.320	57.5	saddle
	Chloroform(2)	0.297		0.190		0.280		
	Methanol(3)	0.440		0.550		0.460		
III-3-2	Methyl acetate(1) Chloroform(2) Benzene(4)	none		none				
III-3-3	Methyl acetate(1) Methanol(3) Benzene(4)	none		none				
III-3-4	Chloroform(2) Methanol(3) Benzene(4)	none		none				

(3) Binary systems

Systems	Components	Reported data mole	Reported data T, ℃	MRSM-2 model Liquid mole	MRSM-2 model Liquid T, ℃	MRSM-2 model Vapor mole	MRSM-2 model Vapor T, ℃	Type of azeotrope
III-2-1	Methyl acetate(1)	0.355	64.8	0.345	65.08	0.339	64.96	max.
	Chloroform(2)	0.645		0.655		0.661		
III-2-2	Methyl acetate(1)	0.672	53.8	0.741	54.69	0.690	54.9	min.
	Methanol(3)	0.328		0.259		0.310		
III-2-3	Methyl acetate(1) Benzene(4)	none		none				
III-2-4	Chloroform(2)	0.650	53.5	0.696	52.95	0.650	54.0	min.
	Methanol(3)	0.350		0.304		0.350		
III-2-5	Chloroform(2) Benzene(4)	none		none				
III-2-6	Methanol(3)	0.610	58.3	0.793	60.34	0.720	60.9	min.
	Benzene(4)	0.390		0.207		0.280		

max: maximum azeotrope

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

$$T=\sum_{i=1}^{N} T_i y_i+\sum_{i\neq j}^{N-1N}\sum A_{ij}\ y_i y_j+\sum_{i\neq j}^{N-1N}\sum B_{ij}\ y_i y_j(y_i-y_j)+\sum_{i\neq j}^{N-1N}\sum C_{ij}\ y_i y_j(y_i-y_j)^2 \quad \text{(for vapor phase)}$$

4. By means of MRSM model, it is possible to predict the temperature of binary, ternary and quaternary system with only normal boiling point of pure components and the binary group-group parameters listed on this paper.

5. Calculated results are in good agreement with experimental data for the selected quaternary systems and their constituent ternaries and binaries. A little deviation was noted in the estimated values for highly nonideal solutions containing the alcohol or volatile organic compound.

6. MRSM methodology, provides a simple procedure for examining existence of azeotropic mixture, type of azeotrope, azeotropic temperature and composition by observing vapor-liquid isothermal contours of ternary and quaternary systems depicted from computer graphics. Two azeotropic mixtures (type, composition, temperature) for two quaternary systems were newly found by this methodology.

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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} : binary interaction parameters of component i & j defined by Eqs. (1)-(3)

N : number of data

T : boiling temperature of mixture

T_i, T_j, T_1, T_2, T_3, T_4 : boiling temperature of pure component i, j, 1, 2, 3, 4

X_i, X_j, X_1, X_2, X_3, X_4 : mole fraction of component i, j, 1, 2, 3, 4 in liquid phase

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

XX, YY : coordinate number on the rectangular coordinate

Greek Letters

α : size factor of the triangle by Eqs.(12), (13)

α, β, γ, δ, ε, η : binary group-group parameter for A_{ij}

α', β', γ', δ', ε', η' : binary group-group parameter for B_{ij}

α'', β'', γ'', δ'', ε'', η'' : binary group-group parameter for C_{ij}

θ_T : parameter defined by Eq. (7)

ϕ_T^A, ϕ_T^B, ϕ_T^C : parameter defined by Eqs. (4), (5) and (6)

Subscripts

exp : exponential

i : component i

j : component j

i-j, i-j-k : i-j pair or i-j-k pair

max. : maximum

min. : minimum

n, n+1 : number of iteration

pre. : predicted

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APPENDIX

Summary of group-group parameters (α, β, γ, δ, ε, η; α', β', γ', δ', ε', η'; α'', β'', γ'', δ'', ε'', η'') for liquid phase and vapor phase of each binary interaction parameters A_{12}, B_{12} and C_{12} for the selected 13 group-groups [2-5, 9].

	Liquid phase						Vapor phase					
		A_{12}		B_{12}		C_{12}		A_{12}		B_{12}		C_{12}
Alcohol-	α	−0.560006	α'	0.389042	α''	−1.194521	α	0.119848	α'	−0.472245	α''	5.671192
Paraffin	β	−0.000144	β'	0.000029	β''	−0.000090	β	0.000120	β'	−0.000265	β''	0.002191
	γ	−0.078169	γ'	0.057533	γ''	−0.160644	γ	0.047971	γ'	−0.099602	γ''	1.020639
	δ	6.741378	δ'	−13.576128	δ''	20.381796	δ	−7.845495	δ'	−3.292597	δ''	−133.191886
	ε	−55.817410	ε'	497.626159	ε''	−407.894259	ε	309.901588	ε'	178.583286	ε''	2364.731487
	η	−271.671706	η'	−4559.943809	η''	3641.282525	η	−2491.91289	η'	−1065.202043	η''	−16428.47658
Alcohol	α	−0.001258	α'	5.241742	α''	−3.276837	α	−2.328973	α'	8.401823	α''	3.278223
Aromatic	β	−0.000405	β'	0.003159	β''	−0.002720	β	−0.001473	β'	0.004652	β''	0.002423
	γ	−0.011556	γ'	1.041554	γ''	−0.682469	γ	−0.449948	γ'	1.642821	γ''	0.672137
	δ	−12.987846	δ'	−88.723888	δ''	38.812280	δ	38.331885	δ'	−155.735577	δ''	−44.685984
	ε	329.312188	ε'	1613.740505	ε''	−608.968938	ε	−689.921990	ε'	2423.973167	ε''	542.250984
	η	−2717.096736	η'	−13500.390799	η''	6436.647152	η	6862.752454	η'	−15015.240829	η''	−4319.573902
Aromatic-	α	6.043312	α'	−2.014979	α''	−2.716525	α	5.497483	α'	6.434403	α''	2.079667
Halogen	β	0.004703	β'	−0.001376	β''	−0.002364	β	0.004220	β'	0.005212	β''	0.001392
	γ	1.241364	γ'	−0.405160	γ''	−0.566624	γ	1.126473	γ'	1.328898	γ''	0.418017
	δ	−88.317003	δ'	31.316354	δ''	40.220833	δ	−81.043505	δ'	−94.080174	δ''	−31.153216
	ε	1048.150816	ε'	−396.189621	ε''	−531.572162	ε	1012.224132	ε'	1163.563061	ε''	360.806335
	η	−5318.760411	η'	2117.753953	η''	2939.979662	η	−5050.559690	η'	−5835.203167	η''	−1522.471855
Aromatic-	α	−23.270161	α'	16.533978	α''	−17.343981	α	−22.739837	α'	−17.133884	α''	−17.073289
Ester	β	−0.022291	β'	0.015622	β''	−0.017335	β	−0.022014	β'	−0.016236	β''	−0.016392
	γ	−4.992249	γ'	3.536463	γ''	−3.760785	γ	−4.890405	γ'	−3.666853	γ''	−3.667330
	δ	306.969041	δ'	−221.220911	δ''	217.955777	δ	297.035083	δ'	229.215147	δ''	223.219430
	ε	−3611.800910	ε'	2646.717743	ε''	−2368.432185	ε	−3403.512190	ε'	−2747.741690	ε''	−2572.816911
	η	19068.714694	η'	−14303.307958	η''	11548.097784	η	17881.630114	η'	15193.774260	η''	13594.956758
Alcohol-	α	−7.371867	α'	121.016739	α''	−162.119342	α	−37.069008	α'	11.402612	α''	98.269519
Halogen	β	−0.003860	β'	0.073431	β''	−0.096927	β	−0.021658	β'	0.007139	β''	0.058388
	γ	−1.386557	γ'	23.501386	γ''	−31.384270	γ	−7.134088	γ'	2.241605	γ''	18.989363
	δ	153.312734	δ'	−2471.139685	δ''	3339.032910	δ	775.956775	δ'	−222.674618	δ''	−2056.853281
	ε	−3068.151735	ε'	51394.970039	ε''	−69715.272320	ε	−16539.062923	ε'	4359.283865	ε''	44105.025307
	η	24851.275632	η'	−482902.424325	η''	654287.064739	η	159342.604938	η'	−40869.445159	η''	−429040.213721
Alcohol-	α	11.936197	α'	−5.472907	α''	16.372178	α	12.142564	α'	5.590163	α''	−1.718955
Ester	β	0.003368	β'	−0.001669	β''	0.004524	β	0.003443	β'	0.001566	β''	−0.000610
	γ	2.100945	γ'	−0.971952	γ''	2.863188	γ	2.139050	γ'	0.979568	γ''	−0.319868
	δ	−358.274894	δ'	153.578868	δ''	−495.472336	δ	−362.246630	δ'	−170.703730	δ''	38.426639
	ε	10640.159930	ε'	−4055.253707	ε''	14691.697118	ε	10704.345212	ε'	5210.972515	ε''	−674.850816
	η	−132516.712695	η'	44070.891427	η''	−179470.870500	η	−130845.205050	η'	−67181.718649	η''	2459.435345

		Liquid phase						Vapor phase					
		A_{12}		B_{12}		C_{12}		A_{12}		B_{12}		C_{12}	
Eester-	α	−2.214814	α′	0.836089	α″	1.217449	α	−1.320981	α′	−0.832012	α″	−1.179817	
Halogen	β	−0.000511	β′	0.000191	β″	0.000248	β	−0.000346	β′	−0.000150	β″	−0.000239	
	γ	−0.420097	γ′	0.159467	γ″	0.224299	γ	−0.260319	γ′	−0.147326	γ″	−0.216898	
	δ	38.396000	δ′	−14.961493	δ″	−21.923779	δ	19.509103	δ′	16.750497	δ″	24.351437	
	ε	−544.833607	ε′	217.570626	ε″	263.874609	ε	−201.97854	ε′	−223.020515	ε″	−404.723337	
	η	2898.226246	η′	−1213.992292	η″	−1203.813023	η	1040.52807	η′	1310.520417	η″	2807.778648	
Ketone-	α	2.252156	α′	1.202463	α″	6.399489	α	0.261475	α′	−16.333964	α″	44.662958	
Paraffin	β	0.000786	β′	0.000268	β″	002240	β	0.000298	β′	−0.004345	β″	0.011604	
	γ	0.428306	γ′	0.205095	γ″	1.185395	γ	0.083826	γ′	−2.862595	γ″	7.789163	
	δ	−57.179896	δ′	−30.693728	δ″	−146.054589	δ	−4.427577	δ′	403.308153	δ″	−1119.335413	
	ε	1114.640602	ε′	816.292109	ε″	2581.079683	ε	37.198508	ε′	−8279.227263	ε″	22753.320020	
	η	−8534.764723	η′	−7119.005162	η″	−17474.242162	η	712.955805	η′	64370.835248	η″	−175615.978361	
Alcohol-	α	0.570674	α′	−1.833134	α″	1.728054	α	0.881896	α′	0.024608	α″	1.259059	
Ketone	β	0.000104	β′	−0.000465	β″	0.000347	β	0.000185	β′	0.000151	β″	0.000314	
	γ	0.103122	γ′	−0.319363	γ″	0.296216	γ	0.157403	γ′	0.015819	γ″	0.217526	
	δ	−17.804209	δ′	50.288269	δ″	−50.395503	δ	−25.927962	δ′	3.203899	δ″	−34.588183	
	ε	388.408640	ε′	−1122.188140	ε″	1216.362831	ε	623.537286	ε′	−184.753782	ε″	823.766202	
	η	−3538.697831	η′	10143.611867	η″	−11632.335726	η	−5198.595439	η′	2709.718961	η″	−8012.800671	
Acid-	α	17.213003	α′	−30.058261	α″	−25.647617	α	−35.356711	α′	26.205931	α″	−31.539656	
Water	β	−0.001068	β′	0.001872	β″	0.001603	β	0.002216	β′	−0.001640	β″	0.001970	
	γ	2.243839	γ′	−3.933000	γ″	−3.356846	γ	−4.640853	γ′	3.434064	γ″	−4.136298	
	δ	−592.557989	δ′	1030.496043	δ″	875.119903	δ	1202.707804	δ′	−892.587002	δ″	1077.595168	
	ε	11008.257318	ε′	−19221.746816	ε″	−16320.029020	ε	−22387.453621	ε′	16569.883657	ε″	−20130.344115	
	η	−68646.758141	η′	120018.569963	η″	101096.732677	η	139427.899938	η′	−102716.817618	η″	124890.267751	
Acid-Acid	α	−0.164828	α′	−0.489583	α″	0.357241	α	−0.074118	α′	−0.656170	α″	−0.438936	
	β	0.015102	β′	−0.068693	β″	−0.301961	β	−0.061686	β′	0.366780	β″	−0.950399	
	γ	0.333217	γ′	−1.594204	γ″	−6.412884	γ	−1.287837	γ′	7.787857	γ″	−20.516087	
	δ	53.224578	δ′	−176.650632	δ″	−775.269257	δ	−142.051653	δ′	957.617505	δ″	−2423.574711	
	ε	−1072.521760	ε′	3317.351808	ε″	13812.246524	ε	2462.809643	ε′	−17169.239659	ε″	43402.431497	
	η	6505.565775	η′	−18765.090126	η″	−74993.546648	η	−12811.672380	η′	93799.266957	η″	−235925.691570	
Aromatic-	α	1.957143	α′	−2.930690	α″	0.336688	α	3.609554	α′	3.313805	α″	−1.630760	
Ketone	β	0.000943	β′	−0.001496	β″	−0.000773	β	0.002007	β′	0.001148	β″	−0.001973	
	γ	0.453881	γ′	−0.692709	γ″	−0.108452	γ	0.888666	γ′	0.675400	γ″	−0.612586	
	δ	−21.141032	δ′	28.586822	δ″	−52.308759	δ	−23.036905	δ′	−50.965906	δ″	−39.872122	
	ε	225.354263	ε′	−323.467808	ε″	1209.078114	ε	81.920693	ε′	697.359058	ε″	1096.945208	
	η	−1491.198423	η′	2302.776844	η″	−8486.155588	η	62.988730	η′	−3906.035039	η″	−7317.377570	