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MODELLING THE EXCESS ENTHALPY FOR TERNARY SYSTEMS FORMED BY ORGANIC COMPOUNDS

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ABSTRACT

The performance of parameter-estimation methods applied to the modelling of experimental binary and ternary excess enthalpy data, namely classical or orthogonal regression, has been compared. For correlation of binary data, the Redlich–Kister equation was used. Ternary data were correlated by two equations: Redlich–Kister or Jones. The data for the system acetone–methanol–chloroform were used as an example. It was demonstrated that these methods are almost equivalent.

INTRODUCTION

The heat of mixing (excess enthalpy) is an important property of a liquid mixture. Besides representing the energetic effects directly connected to the interactions between different molecules, it is important for the description of the thermodynamic properties of phases.

From a practical point of view, the knowledge of the dependence of the excess enthalpy on concentration and temperature is most important. It enables prediction of the temperature dependence of the Gibbs energy. For this reason, the enthalpy of mixing as a function of concentration at constant temperature is widely measured.

The task of this paper is to compare estimation methods and correlating equations used for descriptions of isothermal multicomponent H^E data. As an example, the system acetone–methanol–chloroform was chosen because of its complexity. This system represents all possible behaviours of the heat of mixing as a function of composition of a binary mixture: acetone–methanol has positive values of H^E, acetone–chloroform has negative values and methanol–chloroform has both negative and positive values (S-shaped).

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MODEL EQUATION

The excess enthalpy of an N-component mixture (H_N^E) can be represented as a function of concentration by a general formula

$$H_N^E = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} h_{ij}^E + \sum_{i=1}^{N-2} \sum_{j=i+1}^{N-1} \sum_{k=j+1}^{N} h_{ijk}^E + \ldots \tag{1}$$

where h_{ij}^E are binary terms depending on the concentration of component i in the mixture of components i and j, and on temperature and h_{ijk}^E are ternary terms depending on the concentrations of components i and j in the mixture of components i, j and k, and on temperature.

It is very rare to have a complete set of experimental H^E data for a quaternary mixture. Due to the lack of experimental data representing the temperature dependence of H^E, all data were treated as being isothermal and temperature independent. A complete set would include all data sets of all possible binary, ternary and quaternary mixtures forming a quaternary system. A complete five-component system is not available at all at present. Due to the lack of multicomponent data, the properties of a mixture can only be predicted from binary data alone. In such a case, eqn. (1) reduces to

$$H_N^E = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} h_{ij}^E \tag{2}$$

Due to the lack of experimental information, this investigation is limited to ternary systems only. For such systems, eqn. (1) reduces to the form

$$H_3^E = h_{123}^E + \sum_{i=1}^{2} \sum_{j=i+1}^{3} h_{ij}^E \tag{3}$$

For the prediction of H_N^E by means of eqn. (2), suitable equations representing binary (h_{ij}^E) data are necessary. The present paper assesses the capability of different equations to represent multicomponent data. The Redlich–Kister equation [1] has been proved to be suitable for the representation of binary excess enthalpy data [2,3]. Two properties of this equation are compared: the ability to represent binary data; and the suitability for the prediction of ternary data by means of eqn. (2).

The Redlich–Kister equation for a binary system has the form

$$h_{ij}^E = x_i x_j \sum_{L=1}^{m_{ij}} A_{ijL}(x_i - x_j)^{L-1} \tag{4}$$

where A_{ijL} are adjustable parameters for a binary mixture of components i and j and m_{ij} is the number of adjustable parameters for a binary mixture of components i and j.

The predictive ability of eqn. (2) was compared with the correlation of all available data by eqn. (3). The term h_{123}^{E}, reflecting the ternary interactions, was introduced in eqn. (3) in two forms

$$h_{123}^{E} = x_1 x_2 x_3 \sum_{i=0}^{2} \sum_{j=0}^{3} B_{ij} x_1^i x_2^i \tag{5}$$

and

$$h_{123}^{E} = x_1 x_2 x_3 \sum_{i=0}^{4} \sum_{j=0}^{4} \sum_{k=0}^{4} D_{ijk} x_1^{i/2} x_2^{j/2} x_3^{k/2} \qquad (k \neq 2, 4) \tag{6}$$

where B and D are adjustable parameters.

Equation (5) with 10 adjustable parameters corresponds exactly to the equation proposed by Morris et al. [4]

$$\begin{aligned} h_{123}^{E} = x_1 x_2 x_3 \big(& B_0 + B_1 x_1 + B_2 x_2 + B_3 x_1^2 + B_4 x_2^2 + B_5 x_1 x_2 + B_6 x_1^3 + B_7 x_2^3 \\ & + B_8 x_1^2 x_2 + B_9 x_1 x_2^2 \big) \end{aligned} \tag{7}$$

Equation (6) corresponds exactly to the equation proposed by Jones et al. [5]

$$\begin{aligned} h_{123}^{E} = x_1 x_2 x_3 \big(& D_0 + D_1 x_1^{1/2} + D_2 x_2^{1/2} + D_3 x_3^{1/2} + D_4 x_1 + D_5 x_2 + D_6 x_1^{3/2} \\ & + D_7 x_2^{3/2} + D_8 x_3^{3/2} \big) \end{aligned} \tag{8}$$

DETERMINATION OF PARAMETERS

In the computation procedure, parameters were treated as independent of temperature. The regression procedure for obtaining the numerical values of parameters, with the use of M experimental data sets, represents a non-linear problem solved by minimisation of the sum of squares of the differences between the measured and calculated values of the thermodynamic variables $(x_1, \ldots, x_N, H_{\mathrm{exp}}^{E})$.

In general, the models used can be represented by the formula

$$Y = f(X, C) \tag{9}$$

with:

$$Y = (Y_1, \ldots, Y_{NY})$$

$$X = X(X_1, \ldots, X_{NX}, U_{NX+1}, \ldots, U_{NX+NU})$$

and

$$C = (C_1, \ldots, C_m)$$

where $Y_1, \ldots, Y_{NY}$ are NY dependent variables; $X_1, \ldots, X_{NX}$ are NX error-free independent variables; $U_{NX+1}, \ldots, U_{NX+NU}$ are NU dependent variables, subject to errors; and $C_1, \ldots, C_m$ are m adjustable parameters.

For the reduction of heat of mixing data for a binary mixture when mole fractions are used as concentration variables, the number of variables reduces to one dependent (concentration) and one independent (heat of mixing). For a ternary mixture there are two independent variables, both representing concentration. The composition of liquid phase is treated as an independent variable and the heat of mixing as a dependent one. For the data reduction, two previously described regression methods, "classical" and "orthogonal", were used [6]. The following equations were used for determining the objective functions.

Classical regression

Minimisation of the function $S(C)$

$$S(C)=\sum_{j=1}^{M}\sum_{k=1}^{NY} w_{k,j}\left(Y_{k,j}^{\text{exp}}-Y_{k,j}^{\text{calc}}\right)^2; \qquad w_{k,j}\geqslant 0 \tag{10}$$

where $Y_{k,j}^{\text{calc}}=f_k(X_{1,j}^{\text{exp}},\ldots,X_{NX,j}^{\text{exp}}, C)$.

Orthogonal regression

Minimisation of the function $S(X, C)$

$$S(X, C)=\sum_{j=1}^{M}\left(\sum_{i=1}^{NU} v_{ij}\left(U_{ij}^{\text{exp}}-U_{ij}\right)^2+\sum_{k=1}^{NY} w_{kj}\left(Y_{kj}^{\text{exp}}-Y_{kj}^{\text{calc}}\right)^2\right);$$

$$w_{kj},\ v_{kj}\geqslant 0 \tag{11}$$

where

$$Y_{k,j}^{\text{calc}}=f_k\left(U_{1j},\ldots,U_{NUj}, C\right), \qquad (U\leqslant X)$$

$v_{ij}=1/\sigma^2_{(X_{i,j})}$ and $w_{i,j}=1/\sigma^2_{(Y_{i,j})}$ (weighting factors), σ^2 is the variance of the measured properties, M is the number of experimental data points and U_{ij} are hypothetical true values of the variables.

In "classical regression", all independent variables X (T, temperature, and x, composition) are treated as error free. In the orthogonal regression, temperature is treated as error free and composition is subject to experimental errors. Because of this, temperature does not appear in the equations used. The list of variables and objective functions used in orthogonal regression procedures is given in Table 1.

These equations were used either for binary data only or for sets consisting of binary and ternary data. The correlation results obtained for a ternary mixture by means of both methods were compared to those obtained by reducing binary data only and predicting ternary H^{E} by means of eqn. (2).

For the investigations, the ternary mixture of acetone with methanol and chloroform was chosen because the measurements have a high accuracy and

TABLE 1

Dependent and independent variables used in the orthogonal regression procedure

Number of components	Type of data	Variables		
		Independent $(U_1,\ldots,U_{NU})$ or $(X_1,\ldots,X_{NX})$	Dependent $(Y_1,\ldots,Y_{NY})$	
Binary	H_{12}^E	x_1	H^E	$NY=1$
Ternary	H_{123}^E	x_1, x_2	H^E	$NY=1$
Binary H_{ij}^E and ternary H_{123}^E	H_{12}^E $+H_{13}^E$ $+H_{23}^E$ $+H_{123}^E$	x_1 x_1 x_2 x_1, x_2	H_{12}^E H_{13}^E H_{23}^E H_{123}^E	$NY=4$

there are a large number of experimental points. The three constituent binary systems represent three different types of H^E versus composition curves: negative values of H^E (acetone–chloroform); positive values of H^E (acetone–methanol); and S-shaped values of H^E (chloroform–methanol).

The computed results are reported in Tables 2–8 below. The following formula was used to represent the mean absolute deviations for all dependent and independent variables

$$\delta Z = \frac{1}{M} \sum_{i=1}^{M} \left| Z_i^{\text{exp}} - Z_i^{\text{calc}} \right| \tag{12}$$

with $Z \in (H^E, x_1, x_2)$ for the orthogonal regression and $Z = H^E$ for the classical regression.

A more useful quantity for the comparison of models is the standard deviation given by the following equation

$$s(H^E)(\text{J mol}^{-1}) = \left[\sum_{i=1}^{M} \left(H^{E(\text{exp})} - H^{E(\text{calc})} \right)^2 / (M - m) \right]^{1/2} \tag{13}$$

This value approximates the overall variance of errors.

The number of adjustable parameters was controlled by a statistical criterion (Fisher test) with a given confidence level ($\alpha = 0.05$). The F-test checks the computed ratio s_μ^2/s_ν^2 ($s_\mu^2 > s_\nu^2$) against a critical value $F_{1-\alpha}(\mu, \nu)$, which has the F-distribution with μ and ν degrees of freedom, and α is the confidence level. In addition, the confidence intervals of parameters for the classical regression were calculated analogously, according to Marquardt and Siam [7]. The confidence intervals, based on linearisation, indicate whether the parameters can be interpreted at all. For non-significant parameters the absolute value of the parameter is smaller than the confidence interval for a given confidence level.

DISCUSSION AND CONCLUSIONS

It is well known [2,3] that of the descriptions of systems exhibiting complex heats of mixing the most suitable are the polynomial type of equations, for example Redlich–Kister. To provide an adequate description of the system investigated, it is necessary to use six parameters in the case of a binary system with positive–negative interactions, three parameters in the case of a system with positive H^E values and four parameters in the case of a system with negative H^E values, as can be seen in Tables 2 and 3. The results of correlation for binary data are independent of the estimation method used: the values of the parameters are statistically the same (see Tables 3 and 4). Table 4 also reports the standard errors of correlations.

Prediction of the excess enthalpy of a ternary system using eqn. (2) for the corresponding binary systems is possible with a mean absolute deviation from experimental values of 40 J mol^{-1}. The results are the same irrespective of whether the parameter values are obtained from classical or from orthogonal regression. The results of computations show that for the representation of a complex ternary system with constituent binaries exhibiting negative, positive and negative–positive (S-shaped) H^E values, a term representing ternary interactions is necessary.

TABLE 2

Comparison of the efficiency of the Redlich–Kister equation with different numbers of parameters for binary systems

Number of R–K parameters m	Number of experimental points M	Standard deviation $\delta(H^E)$ (J mol^{-1})	Maximum deviation $\max\|\Delta H^E\|$ (J mol^{-1})	Number of sign changes	Comparison of models (F-test) [a]
Acetone–methanol					
2	20	4.95	8.9	5	+
3	20	0.64	0.9	11	+
4	20	0.65	0.9	11	=
Acetone–chloroform					
3	17	9.08	12.3	3	+
4	17	2.23	4.5	4	+
5	17	1.70	3.3	7	=
Chloroform–methanol					
3	36	34.41	83.8	3	+
4	36	19.91	42.2	4	+
5	36	7.20	18.0	9	+
6	36	4.54	11.1	20	+
7	36	4.24	10.0	20	=

[a] +, Rejection of the null hypothesis (second model is better then the first one); =, models are equivalent.

TABLE 3

Correlation parameters in eqn. (4) for binary systems $(i-j)$ with their standard deviations and their $100(1-\alpha)\%$ confidence intervals ($\alpha = 0.05$) for the classical regression procedure

Types of parameters A_{ijL}	Parameter value and standard deviation	Confidence interval	Parameter value and standard deviation	Confidence interval
Acetone (1)–chloroform (2)				
	R–K with 4 parameters		R–K with 5 parameters	
A_{121}	−7006.0 ± 38.7	138.0	−7000.5 ± 34.2	11.8
A_{122}	1869.0 ± 15.5	55.4	1870.2 ± 11.9	46.8
A_{123}	737.4 ± 18.0	64.0	633.3 ± 35.2	138.9
A_{124}	−570.6 ± 38.5	137.3	−569.8 ± 29.4	116.0
A_{125}	–	–	185.5 ± 57.9	228.3
Acetone (1)–methanol (3)				
	R–K with 3 parameters		R–K with 4 parameters	
A_{131}	3067.6 ± 1.0	3.1	3067.4 ± 1.1	3.9
A_{132}	427.6 ± 2.4	7.5	426.5 ± 4.2	14.7
A_{133}	174.7 ± 5.3	16.5	175.2 ± 5.6	19.5
A_{134}	–	–	3.6 ± 11.3	39.2
Chloroform (2)–methanol (3)				
	R–K with 6 parameters		R–K with 7 parameters	
A_{231}	169.9 ± 7.1	26.8	162.3 ± 7.4	29.9
A_{232}	4690.9 ± 34.8	132.5	4715.1 ± 34.1	138.4
A_{233}	128.8 ± 71.8	273.8	403.6 ± 136	553.5
A_{234}	809.5 ± 200	763.3	708.6 ± 192	779.1
A_{235}	2749.1 ± 119	455.1	1569.3 ± 522	2118.2
A_{236}	1700.9 ± 245	936.3	1776.9 ± 232	940.1
A_{237}	–	–	1157.6 ± 501	2030.3

The accuracy of the representation of ternary interactions by the Redlich–Kister and Jones equations is similar (Tables 5 and 6), leading to almost identical results. In both cases three ternary terms are sufficient for the representation of experimental data with the accuracy of the original experiment. Increasing the number of adjustable parameters does not improve the correlation results. The values ($B_{00} = -3515.3$, $B_{10} = 10042.7$ and $B_{01} = -8068.9$) of the Redlich–Kister parameters obtained by means of the orthogonal method are within a confidence interval half that computed for the classical regression method (Table 7). Both methods of parameter estimation give almost the same results, as can be seen in Table 8. The slightly better results obtained by the orthogonal method are not important from the statistical point of view.

In the calculations, two methods for parameter estimations were used. In both cases, the results were statistically the same; therefore it is better to use

TABLE 4

Correlation parameters in eqn. (4) for the binary systems ($i-j$) and the mean absolute errors of adjustment for the orthogonal regression procedure

System	Type of parameters	Parameter values	Computed errors	
			$\delta x_1 \times 100$	δH^E (J mol^{-1})
Acetone–chloroform	A_{121}	−7002.5		
	A_{122}	1882.3		
	A_{123}	713.4		
	A_{124}	−594.4	0.03	0.8
Acetone–methanol	A_{131}	3067.2		
	A_{132}	428.4		
	A_{133}	179.9	0.02	0.3
Chloroform–methanol	A_{231}	170.0		
	A_{232}	4707.8		
	A_{233}	207.9		
	A_{234}	834.5		
	A_{235}	2477.5		
	A_{236}	1455.5	0.12	1.1

TABLE 5

Influence of the number of adjustable parameters of the Redlich–Kister equation on the computation accuracy of H^E data (experimental values from Morris et al. [4])

Ternary parameters	Computed errors			Comparison of models (F-test) [a] $\alpha = 0.05$
	δH^E (J mol^{-1})	σH^E (J mol^{-1})	max $\mid \Delta H^E \mid$ (J mol^{-1})	
None	39.5 [b]	56.4 [b]	166.6 [b]	–
B_{00}	28.5	36.1	100.5	+
+ B_{10}	18.8	23.6	53.5	+
+ B_{01}	13.2	16.8	52.3	+
+ B_{20}	12.1	16.2	51.5	=
+ B_{02}	10.3	13.7	33.2	=
+ B_{11}	10.2	13.5	30.3	=
+ B_{30}	10.2	13.6	31.4	=
+ B_{03}	10.2	13.5	29.7	=
+ B_{21}	10.2	13.6	30.9	=
+ B_{12}	9.6	12.7	34.4	=
+ B_{31}	9.6	12.7	34.3	=
+ B_{13}	9.6	12.7	35.2	=
+ B_{23}	9.1	12.1	33.6	=
+ B_{32}	9.1	12.1	33.3	=
+ B_{22}	8.8	11.9	35.5	=
+ B_{33}	8.6	11.7	34.3	=

[a] +, Rejection of the null hypothesis (second model is better then the first one); =, models are equivalent.

[b] Difference between predicted and measured values.

TABLE 6

Influence of the number of adjustable parameters of the Jones equation on the computation accuracy of H^E data (experimental values from Morris et al. [4])

Ternary parameters	Computed errors			Comparison of models (F-test) [a] $\alpha = 0.05$
	δH^E (J mol^{-1})	σH^E (J mol^{-1})	max $\lvert \Delta H^E \rvert$ (J mol^{-1})	
none	39.5 [b]	56.4 [b]	166.6 [b]	–
D_{000}	28.5	36.1	100.5	+
$+ D_{100}$	17.8	22.6	43.2	+
$+ D_{010}$	11.4	14.7	40.7	+
$+ D_{001}$	11.4	14.7	39.5	=
$+ D_{200}$	11.0	14.1	35.9	=
$+ D_{020}$	10.3	13.5	34.0	=
$+ D_{300}$	10.1	13.5	34.4	=
$+ D_{030}$	10.1	13.5	33.9	=
$+ D_{003}$	9.2	13.5	29.4	=
$+ D_{400}$	9.2	11.8	29.4	=
$+ D_{040}$	9.0	11.8	31.5	=
$+ D_{004}$	9.0	11.8	30.1	=
$+ D_{220}$	9.0	11.8	29.9	=
$+ D_{440}$	8.6	12.0	30.2	=

[a] +, Rejection of the null hypothesis (second model is better then the first); =, models are equivalent.

[b] Difference between predicted and measured values.

TABLE 7

Ternary correlation parameters in eqns. (5) and (6) for the system acetone–chloroform–methanol with their standard deviations and their 100(1 – α)% confidence interval for the classical regression procedure

Types of parameters	Parameter value and standard deviation	Confidence interval	Parameter value and standard deviation	Confidence interval
Redlich–Kister equation				
	With 3 parameters		With 4 parameters	
B_{00}	-3298.5 ± 339	963.8	-4418.7 ± 463	1451.4
B_{10}	8665.2 ± 616	1748.4	16096.0 ± 2267	7096.7
B_{01}	-6819.0 ± 635	1801.7	6749.2 ± 609	1907.5
B_{20}	–	–	-10497.0 ± 3093	9678.5
Jones equation				
	With 3 parameters		With 4 parameters	
D_{000}	-3835.8 ± 539	1527.4	-94.1 ± 2858	8942.4
D_{100}	9846.6 ± 591	1676.6	7704.8 ± 1711	5355.2
D_{010}	-7800.3 ± 606	1718.2	-9995.0 ± 1754	5487.6
D_{001}	–	–	-2331.9 ± 1749	5473.8

TABLE 8

Influence of the number of adjustable parameters of the Redlich–Kister equation on the computation accuracy of H^E data (experimental values from Morris et al. [4])

Redlich–Kister ternary parameters	Regression type	Errors (eqn. (12))					
		$\delta x_1 \times 100$	$\delta x_2 \times 100$	δH_2^E 1–2	δH_2^E 1–3	δH_2^E 2–3	δH_3^E
B_{00}, B_{10}, B_{01}	Classical	–	–	1.6	0.5	1.1	13.2
$B_{00},\ldots, B_{02}$	Classical	–	–	1.6	0.5	1.1	10.3
$B_{00},\ldots, B_{23}$	Classical	–	–	1.6	0.5	1.1	9.1
B_{00}, B_{10}, B_{01}	Orthogonal	0.10	0.13	2.7	0.8	0.4	4.1
$B_{00},\ldots, B_{02}$	Orthogonal	0.07	0.11	1.1	0.5	0.4	3.3
$B_{00},\ldots, B_{23}$	Orthogonal	0.06	0.10	0.9	0.4	0.4	3.1

the classical method taking into account the mathematical and numerical complexity of the orthogonal regression.

In our opinion the use of orthogonal regression is justified only when the experimental errors are small and well known, and when the model used does not introduce systematic errors. It is difficult to fulfil both of these conditions in the case of enthalpy of mixing measurements.

LIST OF SYMBOLS

A	binary parameters of the Redlich–Kister equation, eqn. (4)
B	ternary parameters in eqn. (5)
D	ternary parameters in eqn. (6)
C	adjustable parameter
H	enthalpy
h	partial enthalpy defined by eqns. (1)–(3)
M	number of experimental data points
m	number of adjustable parameters
N	number of components
NX	number of error-free independent variables
NU	number of independent variables treated with experimental errors
NY	number of dependent variables
s	standard deviation in adjusted model parameters (eqn. (13))
S	sum of the weighted squared deviations defined by eqns. (10) and (11)
U	hypothetical true values of variables
v	weighting factor for independent variables
w	weighting factor for dependent variables
x	mol fraction in the liquid phase

X	vector of independent variables
Y	vector of dependent variables
Z	thermodynamic variable ($Z \in (x_1, x_2, H^E)$)

Greek letters

δ	mean absolute error
σ	estimated value of experimental error (eqn. (11))
Δ	difference between computed and measured value or difference between computed 'true' and measured value

Superscripts

calc	computed value
exp	measured value
E	excess functions

Subscripts

i, j, k	component indices
α	level of significance ($100(1-\alpha)\%$ probability)
μ, ν	number of degrees of freedom

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