Numerical Processing of Ternary Liquid Experimental Data

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Introduction

Matlab program Ternar2, ver. 2.16, carries out fitting of excess volumes values for ternary mixtures. The values of excess volumes were calculated from the experimental data of mixture densities and densities of pure components. The modified Redlich-Kister equation is used for data fitting. This data model can optionally contain different numbers of binary and ternary constants. The optimization is performed using the least squares method in computational environment of the Matlab system with help of Optimization Toolbox functions.

Brief theoretical fundamentals

The V_m^E values were calculated [2] from the mixtures densities, ρ, and the densities, ρ_i, and molar masses, M_i, of pure components i by using the general relation for multicomponent mixture of k component:

$$V_m^E = \sum_{i=1}^{k} x_i M_i (\rho^{-1} - \rho_i^{-1})$$

where subscript i refers to component i of the mixture and x_i stands for the mole fraction of the respective component.

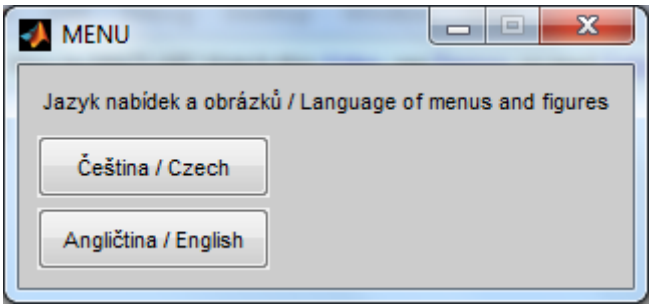
For the ternary system, the Redlich–Kister equation was modified [3] as follows

$$V_m^E = \sum_{i<j} x_i x_j \sum_{k=0}^{n} A_{(ij)k} (x_i - x_j)^k + x_1 x_2 x_3 (B_0 + B_1 x_1 + B_2 x_2 + B_3 x_1^2 + B_4 x_1 x_2 + B_5 x_2)$$

where $A_{(ij)k}$ are binary and B_m ternary disposable parameters. The ternary terms in the equation are usually used in different forms [1]. It was used here a simple and ”transparent” polynomial.

Procedure of digital processing of measured data

- **selection of the language of menus, figures and information messages**



- **entering the name of the data file and reading the data**

```
Input data file
***************

Enter the name of the data file: testdata


Data file testdata.xls was successfully opened!!!
```

- **structure of mixture components data (worksheet Constants)**

Mixture components		
$Comp_1$	**$Comp_2$**	**$Comp_3$**
Molar masses		
M_1	**M_2**	**M_3**
114,200 00	92,100 00	74,100 00
$g.mol^{-1}$	$g.mol^{-1}$	$g.mol^{-1}$
Densities		
ρ_1	ρ_2	ρ_3
0,688 000	0,862 000	0,806 000
$g.cm^{-3}$	$g.cm^{-3}$	$g.cm^{-3}$

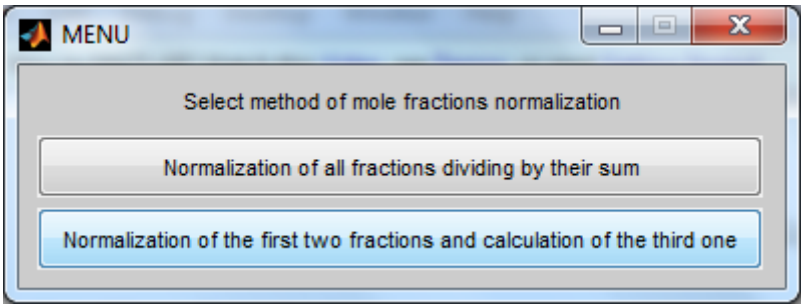
- **reading mixture components data**

```
Reading input data
******************

Names of three components successfully read!!!
1. component: Comp1
2. component: Comp2
3. component: Comp3

Molar masses of three components successfully read!!!
Molar mass of 1. component: 114.2
Molar mass of 2. component: 92.1
Molar mass of 3. component: 74.1

Densities of three components successfully read!!!
Density of 1. component: 0.688
Density of 2. component: 0.862
Density of 3. component: 0.806

Measurement temperature successfully read!!!
Measurement temperature: 298.15
```

- **reading measured values of densities**

```
Measured densities of ternary mixtures successfully read!!!
58 measured points read!!!
```

- **selection of method of mole fractions normalization**



- **structure of experimental measured density data (worksheet Data)**

Comp1	Comp2	Comp3	Temperature	298,15 K
Mole fractions			Density	
x_1	x_2	x_3	ρ	
-	-	-	g.cm^{-3}	
0,00000	1,00000	0,00000	0,86200	
0,13000	0,87000	0,00000	0,82900	
0,26200	0,73800	0,00000	0,80000	
0,40500	0,59500	0,00000	0,77200	
0,52800	0,47200	0,00000	0,75100	
0,66500	0,33500	0,00000	0,73000	
0,79400	0,20600	0,00000	0,71200	
0,92200	0,07800	0,00000	0,69600	
1,00000	0,00000	0,00000	0,68800	
0,96200	0,00000	0,03800	0,69000	
0,90800	0,00000	0,09200	0,69300	
0,80900	0,00000	0,19100	0,70100	

- **writing experimental data**

```
Writing experimental data
*************************

Writing data to output MS Excel tables!!!
Wait, data writing may take tens of seconds!!!

51 rows of measured values written into file testdata.xls successfully!!!
```

- **written processed density and excess molar volume data (part of worksheet Results)**

Comp1	Comp2	Comp3	Temperature	298,15
Mole fractions			Density	Excess volume
x1	x2	x3	r	VEm
-	-	-	g.cm-3	cm3.mol-1
0	0	1	0,806	0
0	0,026	0,974	0,808	-0,035990814
0	0,133	0,867	0,815	-0,06072063
0	0,261	0,739	0,822	0,034564374
0	0,407	0,593	0,831	-0,017913227
0	0,541	0,459	0,838	0,044058733
0	0,671	0,329	0,845	0,046333208
0	0,797	0,203	0,851	0,113837254
0	0,933	0,067	0,858	0,091422641
0	1	0	0,862	0
0,02	0,03	0,95	0,804	-0,030480213
0,021	0,081	0,898	0,807	-0,026481471
0,031	0	0,969	0,799	0,065622527

- **writing calculated values of excess molar volumes**

```
Writing calculated excess volumes
*********************************

Writing data to output MS Excel tables!!!
Wait, data writing may take tens of seconds!!!

51 rows of measured values written into file testdata.xls successfully!!!
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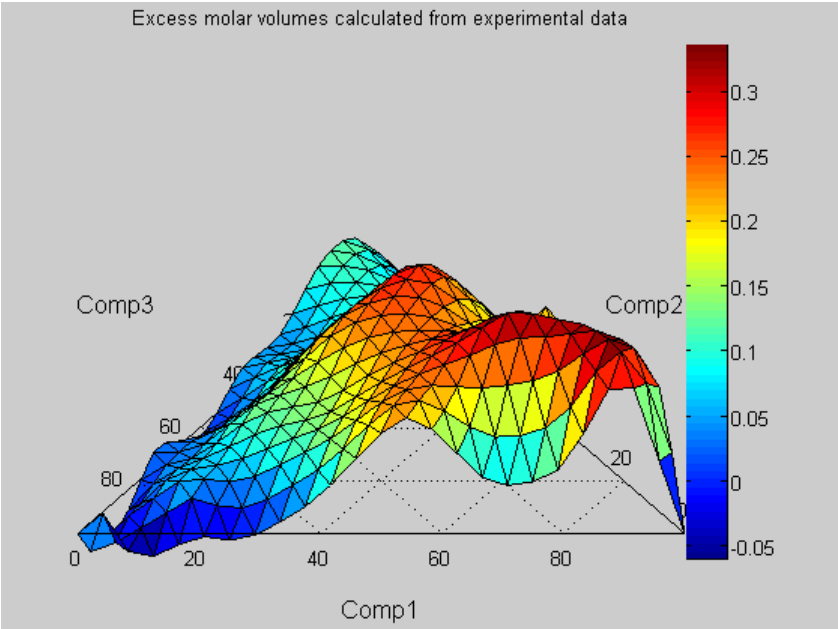
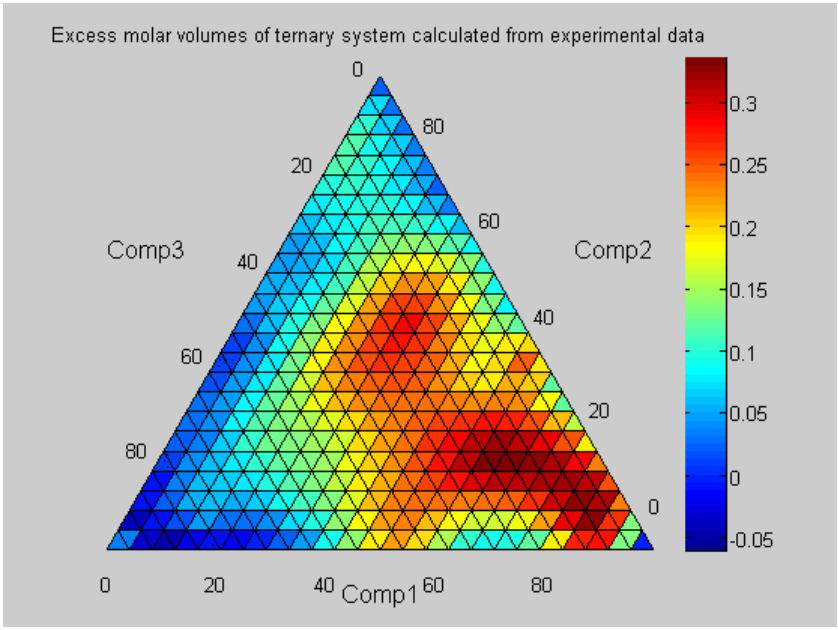
- **visualization of excess molar volumes**





- **entering parameters of modified Redlich-Kister equation**

```
Parameters of modified Redlich-Kister equation
**********************************************

Enter degrees of Redlich-Kister equation binary parts: 2
Enter degree  of Redlich-Kister equation ternary part: 2
```

- **fitting excess molar volumes using modified Redlich-Kister equation by means of least squares method**

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Progress and results of optimization
************************************

Results of calculated data fitting
Sum of error squares          : 1.0025e-01
Maximum error                 : 1.3521e-01
Average error                 : 3.3225e-02
Number of taken iterations    :          18
Number of function evaluations:         304

Optimum reached successfully in     0.6975 s!!!
Change in goal function value is less than 2.2204e-16 !!!
```

- **optimal values of modified Redlich-Kister equation coefficients**

```
Optimum coefficients of modified Redlich-Kister equation
********************************************************

A(1,2)0 =  0.369224
A(1,2)1 =  0.952238
A(1,2)2 =  1.268600
A(1,3)0 =  0.415068
A(1,3)1 =  1.200879
A(1,3)2 =  0.719122
A(2,3)0 =  0.097050
A(2,3)1 =  0.665377
A(2,3)2 =  0.296870
B(0)    =  8.712624
B(1)    = -11.619075
B(2)    = -18.482570
B(3)    = -1.299839
B(4)    =  40.764669
B(5)    =  6.119182
```

- **writing optimal values of modified Redlich-Kister equation coefficient (worksheet Coefficients)**

```
Writing coefficients of modified Redlich-Kister equation
*******************************************************

Writing coefficients to output MS Excel workbook!!!
Wait, data writing may take tens of seconds!!!

15 optimum coefficients of Redlich-Kister equation successfully written to file testdata.xls !!!
```

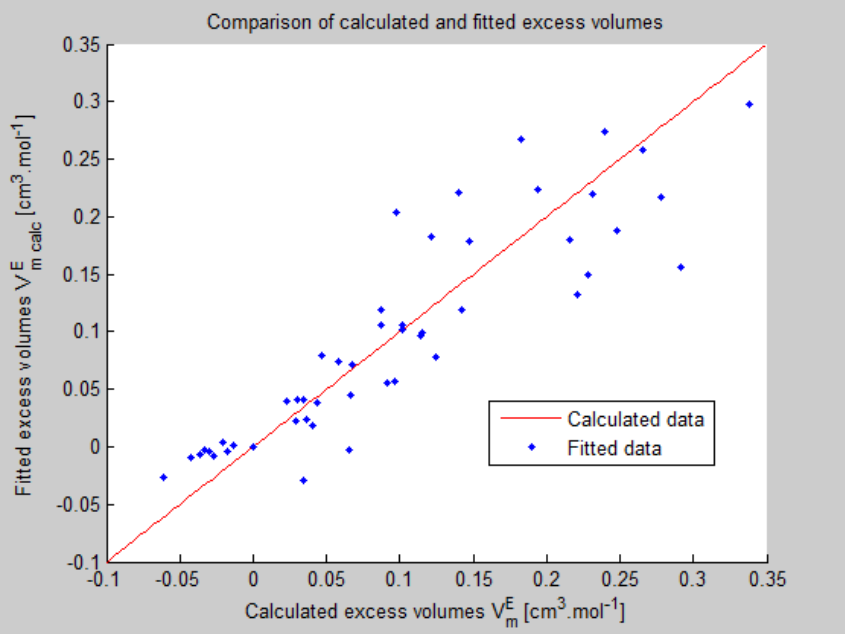
- **written optimum values of modified Redlich-Kister equation (worksheet Coefficients)**

Coefficients of modified Redlich-Kister equation			
binary parts degree	2		
ternary part degree	2		
A(1,2)0	0,36922425		
A(1,2)1	0,95223827		
A(1,2)2	1,26859958		
A(1,3)0	0,41506753		
A(1,3)1	1,20087929		
A(1,3)2	0,71912229		
A(2,3)0	0,09704997		
A(2,3)1	0,66537675		
A(2,3)2	0,2968703		
B(0)	8,71262408		
B(1)	-11,619075		
B(2)	-18,48257		
B(3)	-1,2998392		
B(4)	40,7646687		
B(5)	6,11918209		

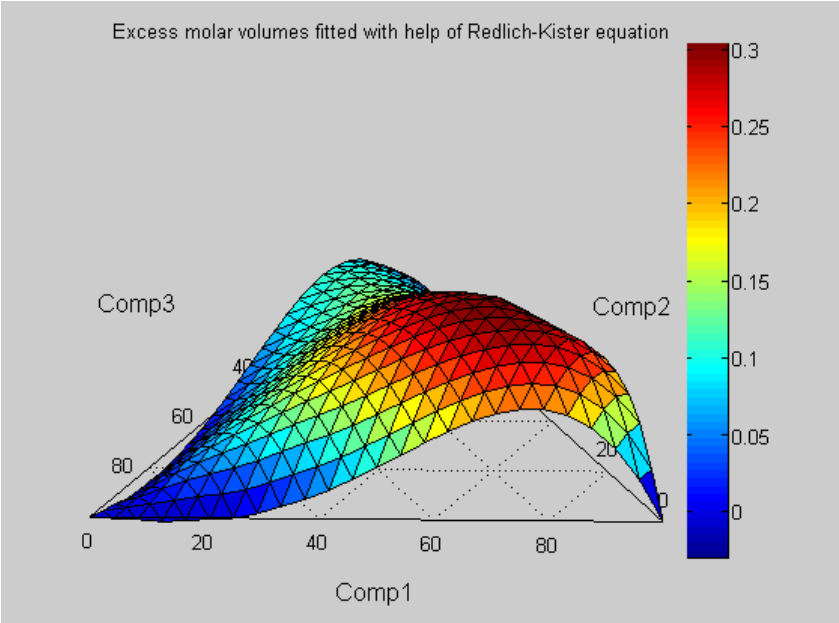
- **writing fitted values of excess molar volumes**

```
Writing fitted excess volumes
*********************************

Writing data to output MS Excel tables!!!
Wait, data writing may take tens of seconds!!!

51 rows of measured values written into file testdata.xls successfully!!!
```

- **graphical comparison of calculated and fitted values of excess molar volumes**



- **visualization of fitted values of excess molar volumes**



- **written values of excess molar volumes calculated from experimental data and fitted using modified Redlich-Kister equation (part of worksheet Results)**

Excess volume	Excess volume
VEm exp	VEm RKe
cm3.mol-1	cm3.mol-1
0	0
-0,035990814	-0,006759701
-0,06072063	-0,026682493
0,034564374	-0,029543277
-0,017913227	-0,003967709
0,044058733	0,038143542
0,046333208	0,079325764
0,113837254	0,096594128
0,091422641	0,056003974
0	0
-0,030480213	-0,004284508
-0,026481471	-0,008317527
0,065622527	-0,002362321
-0,032946517	-0,002226913
0,0288171	0,022491509
-0,020755782	0,003749933
0,036366623	0,024236009
0,058638301	0,074361633
0,03008456	0,04063152
-0,041991688	-0,009283804
0,087307136	0,118577287
0,040600439	0,018069996
0,114868008	0,09962529
0,067399134	0,071644679
0,086674061	0,106068356

References

[1] Kratochvíla, J., Cibulka, I., Holub, R.: Excess volume of the benzene-methanol-acetonitrile ternary mixture at temperatures of 25 and 40 °C and correlation of its concentration dependence. *Collect. Czech. Chem. Commun.*, 45, 12, 3241-3248, 1980.

[2] Morávková, L., Wagner, Z., Sedláková, Z., Linek, J.: Volumetric behaviour of binary and ternary liquid systems composed of ethanol, isooctane, and toluene at temperatures from (298.15 to 328.15) K. Experimental data and correlation. *J. Chem. Thermodynamics*, 43, 12, 1906-1916, 2011.

[3] Morávková, L., Wagner, Z., Sedláková, Z., Linek, J.: Volumetric behaviour of the ternary liquid system composed of methyl *tert*-butyl ether, toluene, and isooctane at temperatures from (298.15 to 328.15) K: Experimental data and correlation. *J. Chem. Thermodynamics*, 42, 7, 920-925, 2010.