MedeA UNIFAC

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1 Key Benefits of *MedeA UNIFAC*

- Determination of geometric descriptors for organic molecules
- Evaluation of activity coefficients for binary mixtures based on Group contributions

2 Introduction

The UNIFAC method (UNIQUAC Functional-group Activity Coefficients) [1] is a group-contribution method for the prediction of activity coefficients in non-electrolyte liquid mixtures. UNIFAC uses the functional groups present in the molecules that make up the liquid mixture, to calculate the activity coefficients based on an extension of the quasi chemical theory of liquid mixtures (UNIQUAC). By using interactions for each of the functional groups present on the molecules, as well as some binary interaction coefficients, the activity of each of the solutions can be calculated. This information can be used to obtain information on liquid equilibria, which is useful in many thermodynamic calculations, such as chemical reactor design, and distillation calculations.

The UNIFAC model was first published in 1975 by Fredenslund, Jones and Prausnitz, a group of chemical engineering researchers from the University of California. Subsequently, they and other authors have published a wide range of UNIFAC papers, extending the capabilities of the model by the development of new or the revision of existing UNIFAC model parameters.

MedeA UNIFAC uses the original UNIFAC description and parameters, as published from 1975 to 2003 [1] [2], [3], [4], [5], [6], [7]. The method and the groups used are described in the rest of this section.

[1] A. Fredenslund, R. L. Jones, J. M. Prausnitz, *"Group-Contribution Estimation of Activity Coefficients in Nonideal Liquid Mixtures"*, AIChE Journal **21**, p. 1086 (1975)

[2] S. Skjold-Jorgensen, B. Kolbe, J. Gmehling and P. Rasmussen, *"Vapor-Liquid Equilibria by UNIFAC Group Contribution. Revision and Extension"*, Ind. Eng. Chem. Process Des. Dev. **18**, p. 714, (1979)

[3] J. Gmehling, P. Rasmussen and A. Fredenslund, *"Vapor=Liquid Equilibria by UNIFAC Group Contribution. Revision and Extension. 2"*, Ind. Eng. Chem. Process Des. Dev. **21**, p. 118 (1982)

[4] E. A. Macedo, U. Weidlich, J. Gmehling and P. Rasmussen, *"Vapor-liquid equilibriums by UNIFAC group contribution. Revision and extension. 3"*, Ind. Eng. Chem. Process Des. Dev. **2**, p. 676 (1983)

[5] D. Tiegs, J. Gmehling, P. Rasmussen, A. Fredenslund, *"Vapor-Liquid Equilibria by UNIFAC Group Contribution. 4. Revision and Extension"*, Ind. Eng. Chem. Res. **26**, p. 159 (1987)

[6] H. K. Hansen, P. Rasmussen, A. Fredenslund, M. Schiller, J. Gmehling, *"Vapor-Liquid Equilibria by UNIFAC Group Contribution. 5. Revision and Extension"*, Ind. Eng. Chem. Res **30**, p. 2352 (1991

[7] R. Wittig, J. Lohmann, J. Gmehling, *"Vapor-Liquid Equilibria by UNIFAC Group Contribution. 6. Revision and Extension"*, Ind. Eng. Chem. Res. **42**, p. 183 (2003)

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3 Method

In a multicomponent mixture, the UNIQUAC equation for the activity coefficient of (molecular) component *i* is:

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \tag{1}$$

where

$$\ln \gamma_i^C = \ln \frac{\Phi_i}{x_i} + \frac{z}{2} q_i \ln \frac{\theta_i}{\Phi_i} + l_i - \frac{\Phi_i}{x_i} \sum_j x_j l_j \tag{2}$$

and

$$\gamma_i^R = q_i \left[1 - \ln \sum_j \theta_j \tau_{ji} - \sum_j \left(\theta_j \tau_{ij} / \sum_k \theta_k \tau_{kj} \right) \right]$$

$$l_i = \frac{z}{2}(r_i - q_i) - (r_i - 1) \quad ; \quad z = 10$$

$$\theta_i = \frac{q_i x_i}{\sum_j q_j x_j} \quad ; \quad \Phi_i = \frac{r_i x_i}{\sum_j r_j x_j}$$

$$\tau_{ji} = \exp - \left[\frac{u_{ij} - u_{ii}}{RT} \right] \tag{3}$$

where x_i is the mole fraction of component *i*, and the summations in equations (2) and (3) are over all components, including component *i*; θ_i is the area fraction, and Φ_i is the segment fraction which is similar to the volume fraction. Pure component parameters r_i and q_i are, respectively, measures of molecular van der Waals volumes and molecular surface areas.

Parameters r_i and q_i are calculated as the sum of the group volume and area parameters R_k and Q_k, given in table Table 1:

$$r_i = \sum_k \nu_k^i R_k \quad and \quad q_i = \sum_k \nu_k^i Q_k \tag{4}$$

where ν_k^i, always an integer, is the number of groups of type *k* in molecule *i*.

The residual part of the activity coefficient, Eq. (3), is replaced by the solution-of-groups concept. Instead of (3), we write:

$$\ln \gamma_i^R = \sum_k \nu_k^{(i)} [\ln \Gamma_k - \ln \Gamma_k^{(i)}] \tag{5}$$

where Γ_k is the group residual activity coefficient, and $\Gamma_k^{(i)}$ is the residual activity coefficient of group k in a reference solution containing only molecules of type *i*.

Note: In Eq. (5) the term $\ln \Gamma_k^{(i)}$ is necessary to attain the normalization that activity coefficient γ_i becomes unity as $x_i \to 1$.

The group activity coefficient Γ_k is found from an expression similar to Eq. (3):

$$\ln \Gamma_k = Q_k \left[1 - \ln \sum_m \Theta_m \Psi_{mk} - \sum_m (\Theta_m \Psi_{km} / \sum_n \Theta_n \Psi_{nm}) \right] \tag{6}$$

Eq. (6) also holds for $\ln \Gamma_k^{(i)}$. In Eq. (5), Θ_m is the area fraction of group *m*, and the sums are overl all different groups. Θ_m is calculated in a manner similar to that for θ_i:

$$\Theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n} \tag{7}$$

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where X_m is the mole fraction of group m in the mixture.

The group interaction parameter Φ_{mn} is given by:

$$\Psi_{mn} = \exp - \left[\frac{U_{mn} - U_{nn}}{RT} \right] = exp - (\alpha_{mn}/T) \tag{8}$$

where U_{mn} is a measure of the energy of interaction between groups m and n. The group-interaction parameters α_{mn} (two parameters per binary mixture of groups) are the parameters that have been evaluated from experimental phase equilibrium data.

Note: α_{mn} has units of degrees Kelvin and $\alpha_{mn} \neq \alpha_{nm}$.

The UNIQUAC model also serves as the basis of the development of the group contribution method UNIFAC, where molecules are subdivided into functional groups. In fact, UNIQUAC is equal to UNIFAC for mixtures of molecules, which are not subdivided; e.g. the binary systems water-methanol, methanol-acryonitrile and formaldehyde-DMF.

4 UNIFAC groups

Table1: Groups and subgrous used in *MedeA UNIFAC*

Group	Subgroup	Name	Description
1			
	1A	CH3	end group of hydrocarbon chain
	1B	CH2	middle group in hydrocarbon chain
	1C	CH	middle group in hydrocarbon chain
	1D	C	middle C in hydrocarbon chain
2			
	2A	CH2=CH2	α-olefins, CH2=CH group
	2B	CH=CH	olefin CH=CH group
	2C	CH=C	olefin CH=C group
	2D	CH2=C	α-olefins, CH2=C group
	2E	C=C	α-olefins, C=C group
3			
	3A	ACH	aromatic carbon group
	3B	AC	aromatic carbon with a branch
4			
	4A	ACCH3	toluene group
	4B	ACCH2	aromatic carbon - alkane group: general case
	4C	ACCH	aromatic carbon bonded to a CH group
5			
	5A	OH	OH in alcohols
6			
	6A	CH3OH	methanol
7			
	7A	H2O	water
8			
	8A	ACOH	aromatic carbon-alcohol group
9			
	9A	CH3CO	carbonyl group in ketones, includes nearest CH3
	9B	CH2CO	carbonyl group in ketones, includes nearest CH2
10			

Table 1 – continued from previous page

Group	Subgroup	Name	Description
	10A	CHO	aldehyde group
11			
	11A	CH3COO	ester group, including CH3 bonded with carbonyl C
	11B	CH2COO	ester group, including CH2 bonded with carbonyl C
12			
	12A	HCOO	formate group
13			
	13A	CH3O	O, in ethers, including nearest CH3
	13B	CH2O	O, in ethers, including nearest CH2
	13C	CHO	O, in ethers, including nearest CH
	13D	THF	tetrahydrofuran
14			
	14A	CH3NH2	methylamine
	14B	CH2NH2	primary amine group, includes nearest CH2
	14C	CHNH2	primary amine group, includes nearest CH
15			
	15A	CH3NH	secondary amine group, includes nearest CH3
	15B	CH2NH	secondary amine group, includes nearest CH2
	15C	CHNH	secondary amine group, includes nearest CH
16			
	16A	CH3N	tetriary amine group, includes nearest CH3
	16B	CH2N	tertiary amine group, includes nearest CH2
17			
	17A	ACNH2	aromatic carbon-amine group
18			
	18A	C5H5N	pyridine
	18B	C5H4N	pyrridine with 1 branch
	18C	C5H3N	pyrridine with 2 branches
19			
	19A	CH3CN	nitrile group, includes nearest CH3
	19B	CH2CN	nitrile group, includes nearest CH2
20			
	20A	COOH	carboxyl group
	20B	HCOOH	formic acid
21			
	21A	CH2CL	chlorine, includes nearest CH2 group
	21B	CHCL	chlorine, includes nearest CH group
	21C	CCL	chlorine, includes nearest C group
22			
	22A	CH2CL2	CH2Cl2 group
	22B	CHCL2	CHCl2 group
	22C	CCL2	CCl2 group
23			
	23A	CHCL3	chloroform
	23B	CCL3	CCl3 group
24			
	24A	CCL4	tetrachloro-methane
25			
	25A	ACCL	aromatic carbon-chloride group
26			

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Group	Subgroup	Name	Description
	26A	CH3NO2	nitro group, includes nearest CH3
	26B	CH2NO2	nitro group, includes nearest CH2
	26C	CHNO2	nitro group, includes nearest CH
27			
	27A	ACNO2	nitro group attached to an aromatic carbon
28			
	28A	CS2	carbon disulfide
29			
	29A	CH3SH	methanethiol
	29B	CH2SH	thiol, includes nearest CH2 group
30			
	30A	FURFURAL	furfural
31			
	31A	DOH	two CH2OH groups
32			
	32A	I	iodine
33			
	33A	Br	bromine
34			
	34A	CH=-C	α-alkynes
	34B	C=-C	alkynes (triple bond not in α position)
35			
	35A	DMSO	dimethylsulfoxide
36			
	36A	ACRY	acrylonitrile
37			
	37A	Cl(C=C)	chloro-olefins, includes C=C group
38			
	38A	ACF	aromatic carbon-fluorine group
39			
	39A	DMF	dimethylformamide
	39B	HCON(CH2)2	
40			
	40A	CF3	CF3 group
	40B	CF2	CF2 group
	40C	CF	CF group
41			
	41A	COO	ester group (recommended for acrylates and benzoates)
42			
	42A	SIH3	methylsilane
	42B	SIH2	silanes (only SiH2 group)
	42C	SIH	
	42D	SI	
43			
	43A	SIH2O	
	43B	SIHO	
	43C	SIO	
44			
	44A	NMP	N-methylpyrrolidone
45			
	45A	CCL3F	trochlorofluoromethane
	45B	CCL2F	

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Table 1 – continued from previous page

Group	Subgroup	Name	Description
	45C	HCCL2F	
	45D	HCCLF	
	45E	CCLF2	
	45F	HCCLF2	
	45G	CCLF3	
	45H	CCL2F2	
46			
	46A	CONH2	
	46B	CONHCH3	
	46C	CONHCH2	
	46D	CON(CH3)2	
	46E	CONCH3CH2	
	46F	CON(CH2)2	
47			
	47A	C2H5O2	
	47B	C2H4O2	
48			
	48A	CH3S	sulfide, includes one nearest CH3 group
	48B	CH2S	sulfide, includes one nearest CH2 group
	48C	CHS	sulfide, includes one nearest CH group
49			
	49A	MORPH	morpholine
50			
	50A	C4H4S	thiophene
	50B	C4H3S	thiophene with 1 branch
	50C	C4H2S	thiophene with 2 branches
51			
	51A	NCO	
55			
	55A	(CH2)2SU	
	55B	CH2CHSU	
84			
	84A	IMIDAZOL	
85			
	85A	BTI	

5 Activity coefficients calculation

MedeA UNIFAC is an interactive tool, providing an easy and quick calculation of activity coefficients of binary mixtures.

The *UNIFAC* GUI can be accessed through Tools >> UNIFAC . The two components can be added directly from *MedeA* or from a saved file and the activity coefficients are calculated for the binary mixture at either constant temperature or constant composition.

At constant temperature, a range of compositions can be explored, providing the lower and upper limits of the composition range (in molar fraction) and the composition increment.
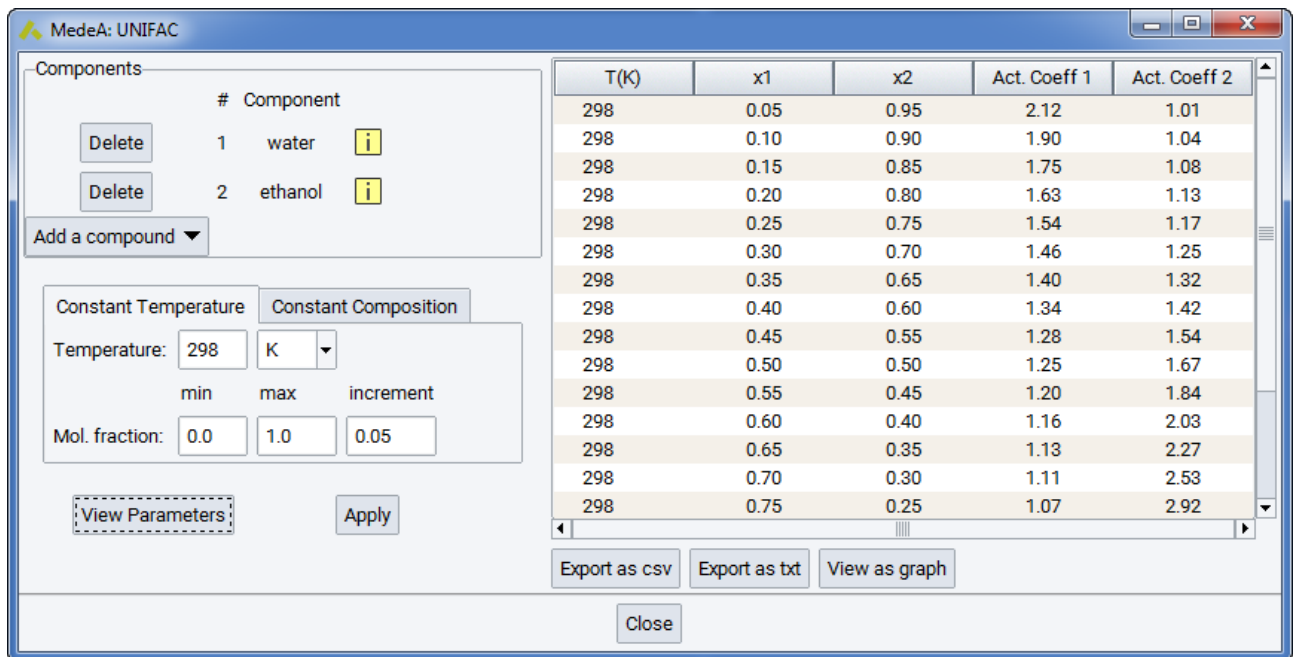
At constant composition, a range of temperatures can be explored, providing the lower and upper limits of the temperature range (in Kelvin, Celsius or Fahrenheit) and the temperature increment.

The output comprises:

- a table with data for temperature, composition and activity coefficients

- *csv* and/or *txt* formated output of the table

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- a graph that can be viewed from within *MedeA*

For example, at a constant temperature, for a mixture of water and ethanol the *MedeA UNIFAC* GUI reports the table with all data on activity coefficients:

A graph is available, showing the activity coefficients as a function of the molecular fraction: