ETHANOL AND DISTILLATE BLENDS: A THERMODYNAMIC APPROACH TO MISCIBILITY ISSUES. PART 2: THE INFLUENCE OF WATER

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ABSTRACT

In recent years, the quest for sustainable primary energies has increased the potential interest of biogenic/fossil fuels mixes. As an example, ethanol is used as a gasoline extender to both partly substitute hydrocarbons and increase octane number while improving vehicle emissions.

In a previous paper (GT2010-22126), it has been shown that ethanol and gasoil are able to blend and form homogeneous solutions only in limited proportion ranges, due to their markedly different physical and chemical properties. However the incorporation of small amounts of water in ethanol dramatically decreases this already narrow miscibility domain. Indeed, in function of the temperature, such ternary mixtures often give rise to liquid-liquid equilibria i.e. to two separated phases that are respectively lipophilic and hydrophilic. A key parameter is thus the Minimum Miscibility Temperature, i.e. the temperature above which ethanol, water and gasoil become completely miscible.

On another hand, commercial gasoils do not constitute a single product but display worldwide a large range of compositions that influence the stability of these ternary blends. In this context, an investigation program intended to characterize and predict the stability of ternary ethanol + water + gasoil blends has been carried out by the LRGP laboratory (Laboratoire Réactions et Génie des Procédés). The approach is based on a thermodynamical, theoretical calculation of the liquid-liquid phase diagrams formed by ethanol, water and a mixture of various hydrocarbons representative of the diesel oil pool using the group-contribution concept. The basic idea is that whereas there are thousands of chemical compounds, the number of functional groups that constitute these compounds is much smaller. The work relies on the experimentally verified theory that a physical property of a fluid can be expressed as the sum of contributions made by molecule's functional groups, which allows correlating the properties of a very large number of substances in terms of a much smaller number of parameters that represent the contributions of individual groups.

This work shows the huge influence exerted by the water content of ethanol on the shape of the liquid-liquid phase diagram and on the value of the Minimum Miscibility Temperature (MMT). As seen in our previous paper, the paraffinic, aromatic or naphthenic character of the fossil fraction, also considerably influences the value of the MMT. Calculations were performed with a water content varying between 1 and 10 %. This study concludes that the MMT expressed in kelvins is generally multiplied by two when the water content rises from 1 to 10 %.

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INTRODUCTION

Industrial ethanol always contains a non negligible amount of water. The goal of this paper is thus to study the influence of the water content of ethanol on the mutual solubility of industrial ethanol and gasoils. Moreover, we want to understand how the proportions of some chemicals (paraffinic compounds, aromatic compounds, naphthenic compounds and sulfur compounds) are likely to influence the miscibility of gasoil + industrial ethanol mixtures and may lead these fluids to unmix. Since quite a few experimental data are available in the openliterature for such complex systems, this kind of study is rather difficult to undertake.

In the present work, starting from the actual composition of some real gasoils mixed with industrial ethanol, we have investigated the miscibility domain of such blends according to the proportion of non anhydrous ethanol contained in them. The ethanol water content was varied between zero and ten % in order to study its influence. To easily compare the miscibility character of various gasoil + ethanol + water mixtures, it is quite convenient to evaluate the so-called *Minimum Miscibility Temperature* (MMT) which is the lowest temperature at which the fluids are completely miscible, regardless of the proportion of industrial ethanol. For any temperature below the MMT, addition of industrial ethanol may give rise to two liquid phases in equilibrium; for any temperature above the MMT, the mixture cannot unmix anymore.

For estimating the MMT of various industrial ethanol + gasoil blends, it was thus necessary to by-pass the lack of data in the open-literature. To do so, we decided to consider an efficient predictive thermodynamic model (called UNIFAC) for representing the behavior of the fluids of interest. This model relies on the group-contribution concept and thus should be able to catch the qualitative effect of the addition of small amounts of water in the alcohol.

USE OF THE GROUP-CONTRIBUTION CONCEPT TO PREDICT THERMODYNAMIC PROPERTIES

General aspects

The group-contribution (GC) approach is a relatively recent concept [1-16] (around fifty years old) allowing prediction of physical properties of a pure molecule or a mixture of molecules, from the knowledge of their chemical structures. Since the nineties and due to the decrease of computation time, methods involving this concept have gained more and more popularity [17].

Within the GC approach, it is assumed that all macroscopic properties are related to molecular structure and the bonds between atoms, which determine the magnitude and predominant type of the intermolecular forces. The relevant characteristics of structure are related to the atoms, atomic groups, bond type, etc. Weighting factors are assigned to them. In most of the widely applied GC methods, molecules are considered as aggregates of atomic groups (see for instance the GC methods proposed by Constantinou and Gani [2], Joback [1], Marrero and Gani [1] and so on). It may be however noticed that some very recent methods exist in which, each atom of a molecule brings its own contribution (atomic groups are replaced by atoms themselves). This is the case within connectivity index methods for instance [16].

In this paper, only classical GC methods (involving atomic groups) are considered. To predict the property Y of a single molecule, a simple summation of the contributions from the molecule's parts is generally used to assess f(Y), a function of Y (for instance Y, ln Y, 1/Y, etc.):

$$f(Y) = \sum_{i=1}^{N_{groups}} C_i G_i$$

In the previous equation, G_i accounts for the total number of groups i present in the considered molecule (in other words, G_i is the occurrence of group i in the molecule). The term C_i is a weighting factor, as mentioned above, called contribution of group i. N_{groups} is the total number of different groups defined by the GC method.

Estimating activity coefficient from GC methods

The application of the GC concept to mixtures is actually an extension of the GC concept for single molecules [3,18]. In any group-contribution method, the basic idea is that whereas there are thousands of chemical compounds of interest in chemical technology, the number of functional groups that constitute these compounds is much smaller. Assuming that a physical property of a fluid is the sum of contributions made by the molecule's functional groups, GC methods allow for correlating the properties of a very large number of fluids using a much smaller number of parameters. These GC parameters characterize the contributions of individual groups in the properties. In this paper, a predictive thermodynamic model based on the GC concept, namely UNIFAC, is used for calculating liquid-liquid phase equilibria of complex gasoil + ethanol + water mixtures. This model allows the estimation of the complete sets of activity coefficients of all the components in a mixture, without fitting any model parameter on liquidliquid experimental data. The mere knowledge of the chemical structure of all the compounds in the mixture is enough to predict phase equilibria. Since the model applies to multicomponent mixtures, it employs a more complex mathematical form than GC models developed for pure molecules.

THE UNIFAC MODEL

The UNIFAC model [18] is a GC method to estimate the activity coefficients of a solution of groups. Based on the

Group k	R _k	Q_k
H ₂ O	0.9200	1.40
CH ₃ -	0.9011	0.848
CH ₂ -	0.6744	0.540
OH-	1	1.2
ArCH-	0.5313	0.4
ArC-	0.3652	0.120
ArCH-CH ₂ -	1.0396	0.66

Table 1. Group contribution parameters R_k and Q_k (as estimated by Bondi et al.) allowing to calculate parameters r_i and q_i of moleculesi involved in ethanol + water + gasoil mixtures. Note: "Ar" means aromatic.

mathematical formulation of the non-predictive UNIQUAC model, the UNIFAC model can be seen as a predictive version of this last model. The UNIQUAC equation often gives good representation of vapor-liquid and liquid-liquid equilibria for binary and multicomponent mixtures containing a variety of non-electrolytes, such as for instance hydrocarbons and alcohols. The molecular activity coefficient is separated into two parts: one part provides the contribution due to differences in molecular size and shape (the combinatorial part), and the other provides the contribution due to molecular interactions (the residual part). In a multicomponent mixture, the UNIFAC equation for the activity coefficient of component i is:

$$\ln \gamma_i = \ln \gamma_i^{\text{comb}} + \ln \gamma_i^{\text{res}}$$

The combinatorial part is estimated using the following equations:

$$\ln \gamma_i^{\text{comb}} = \ln \left(\frac{\varphi_i}{x_i} \right) + \frac{z}{2} \cdot q_i \cdot \ln \left(\frac{\theta_i}{\varphi_i} \right) + L_i - \frac{\varphi_i}{x_i} \sum_{j=1}^p x_j L_j$$
$$\varphi_i = \frac{r_i \cdot x_i}{\sum_{j=1}^p r_j \cdot x_j} \quad ; \quad \theta_i = \frac{q_i \cdot x_i}{\sum_{j=1}^p q_j \cdot x_j}$$

$$L_{i} = \frac{z}{2} (r_{i} - q_{i}) - (r_{i} - 1)$$
$$z = 10$$

where x_i is the mole fraction of component i in a mixture containing p components. The calculation of $\ln \gamma_i^{comb}$ requires the knowledge of pure-component parameters r_i and q_i that are respectively the molecular Van der Waals volume and molecular surface areas. These parameters are calculated using GC methods according to:

$$\begin{cases} r_i = \sum_{k=1}^{NGS} \nu_k^{(i)} R_k \\ q_i = \sum_{k=1}^{NGS} \nu_k^{(i)} Q_k \end{cases} \end{cases}$$

with:

• R_k:

• Q_k :

• NGS: total number of groups defined in the method,

• $v_k^{(i)}$: occurrence of group k in molecule i,

- contribution of group k in the r-property,
- contribution of group k in the q-property.

		Group n			
		CH ₂ -	OH-	ArCH–	ArCH–CH ₂ –
th m	CH ₂ -	0	644.6	-114.8	-115.7
	OH-	328.2	0	-9.210	1.270
Grou	ArCH-	156.5	703.9	0	167
	ArCH–CH ₂ –	104.4	4000	-146.8	0

 Table 2. Group contributions parameters a_{mn} (as estimated by Fredenslund et al.) of the UNIFAC model allowing to quantify group interactions in ethanol + gasoil mixtures. Note: "Ar" means aromatic.

		Group n			
		CH ₂ -	OH-	ArCH–	ArCH–CH ₂ –
	CH ₂ -	0	644.6	-114.8	-115.7
ıp m	OH-	125.59	0	-9.210	1.270
Grot	ArCH-	156.5	447.46	0	167
	ArCH–CH ₂ –	104.4	2993.6	-146.8	0

 Table 3. Group contributions parameters a_{mn} of the UNIFAC model allowing to quantify group interactions in ethanol + gasoil mixtures. Bold values were recalculated in this work. The other ones were estimated by Fredenslund et al.

Numerical values of parameters R_k and Q_k were initially estimated by Bondi et al. [19]. Some selected values of these two parameters are provided in table 1 for groups k involved in mixtures of ethanol, gasoil and water.

The residual part of the activity coefficient in the UNIFAC model is also calculated using a GC method according to the following equation:

$$\begin{split} \ln \gamma_{i}^{res} &= \sum_{k=1}^{NGS} \nu_{k}^{(i)} \Big[\ln \Gamma_{k} - \ln \Gamma_{k}^{(i)} \Big] \\ \ln \Gamma_{k} &= Q_{k} \Bigg[1 - \ln \Bigg(\sum_{j=1}^{NGS} \theta_{j} \psi_{jk} \Bigg) - \sum_{j=1}^{NGS} \frac{\theta_{j} \psi_{kj}}{\sum_{\ell=1}^{S} \theta_{\ell} \psi_{\ell j}} \Bigg] ; \\ \ln \Gamma_{k}^{(i)} &= Q_{k} \Bigg[1 - \ln \Bigg(\sum_{j=1}^{NGS} \theta_{j}^{(i)} \psi_{jk} \Bigg) - \sum_{j=1}^{NGS} \frac{\theta_{j}^{(i)} \psi_{kj}}{\sum_{l=1}^{NGS} \theta_{l}^{(i)} \psi_{lj}} \Bigg] \\ &= \frac{Q_{j} X_{j}}{\sum_{k=1}^{NGS} Q_{k} X_{k}} ; X_{k} = \frac{\sum_{i=1}^{p} x_{i} v_{k}^{(i)}}{\sum_{j=1}^{p} x_{i} \left(\sum_{j=1}^{NGS} v_{j}^{(i)} \right)} ; \psi_{jk} = \exp \Bigg(-\frac{a_{m_{j} n_{k}}}{T} \Bigg) \\ &\qquad \theta_{j}^{(i)} = \frac{Q_{j} X_{j}^{(i)}}{\sum_{k=1}^{NGS} Q_{k} X_{k}^{(i)}} ; X_{k}^{(i)} = \frac{v_{k}^{(i)}}{\sum_{j=1}^{NGS} v_{j}^{(i)}} \end{split}$$

 $\boldsymbol{\theta}_{j}$

The calculation of $\ln \gamma_i^{res}$ requires the knowledge of energy group-interaction parameters a_{mn} , the values of which were estimated from phase equilibrium data regression by Fredenslund et al. [18]. Some a_{mn} -values are provided in table 2 for selected groups involved in gasoil + ethanol mixtures.

RECALCULATION OF ENERGY PARAMETERS A_{MN} OF THE UNIFAC MODEL IN ORDER TO IMPROVE THE PREDICTION OF MINIMUM MISCIBILITY TEMPERATURES

Context

As explained in the introduction, this work is dedicated to the prediction of minimum miscibility temperatures (MMT) of complex ethanol + gasoil + water fluids containing several dozens of various hydrocarbons. As a consequence, the use of classical g^E-models (Van Laar, Margules, Redlich-Kister, NRTL, UNIQUAC and so on) for calculating these temperatures becomes very difficult if not impossible since it would require the knowledge of complete sets of g^E-model parameters A_{ij} (the A_{ij} parameter quantifies the binary interaction between molecules i and j). These parameters A_{ij} are available in the open-literature for a reduced number of systems. In addition, they can be estimated only when reliable fluid phase equilibrium data exist.

To overcome this limitation, it was decided to only consider the predictive UNIFAC g^{E} -model. Let us note that the use of a predictive g^{E} -model allows a significant reduction of the number of model parameters with respect to non-predictive g^{E} -models. To use the UNIFAC model, the mere knowledge of group-contribution parameters is required.

However, like for any predictive model, developers of the UNIFAC model have originally estimated the group contributions parameters in order to minimize the deviations between calculated and experimental equilibrium data for the largest possible variety of mixtures. In other words, it means that the group-contribution parameters estimated by Fredenslund et al. are not only supposed to give good predictions for ethanol + gasoil + water systems, but also for all the other mixtures involving at least the same UNIFAC groups. As a consequence, the values of the a_{mn} -parameters proposed by Fredenslund et al., are not the most appropriate ones to predict minimum miscibility temperatures of ethanol + gasoil + water mixtures. As an illustration, let us consider the binary system: ethanol + n-dodecane. Using the original UNIFAC model, the

Binary system	Original UNIFAC	Modified UNIFAC	Experimental value
n-dodecane / ethanol	65 °C	13 °C	13 °C
dodecyl- benzene / ethanol	75 °C	15 °C	28 °C
Octadecyl- naphthalene / ethanol	185 °C	100 °C	93 °C

Table 4. Prediction of minimum miscibility temperature for three selected binary systems using original UNIFAC and modified UNIFAC (this work). Comparison with experimental values.

minimum miscibility temperature is predicted around 65 °C (let us note that for binary systems, the minimum miscibility temperature is the Upper Critical Solution Temperature, UCST). Actually, experimental measurements allow to estimate this temperature at 13 °C. This example points out very clearly that the UNIFAC model is not able to properly predict this MMT using the original set of UNIFAC GC parameters. It thus seems that a better accuracy could be reached by readjusting some GC parameters using only experimental data for systems containing ethanol and molecules issued from the gasoil cut.

Recalculation of new GC parameters of the UNIFAC model

In order to improve the prediction of ethanol + gasoil systems with the UNIFAC model, it was decided to select three binary hydrocarbon + ethanol systems [20, 21]: n-dodecane + ethanol, dodecylbenzene + ethanol, octadecylnaphthalene + ethanol. Interactions within these three binary systems are deemed as well representative of interactions found within ethanol + gasoil blends. In addition, many a_{mn} -UNIFAC parameters are used to model gasoil + ethanol mixtures, as explained previously (see table 2). After having carefully studied the influence of each of all these parameters on the shape of the liquid-liquid equilibrium curves for the three aforementioned binary systems, it was decided to only change

three parameters among the twelve ones: $a_{OH/CH2}$, $a_{ArCH/OH}$ and $a_{ArCHCH2/OH}$. To do so, we have considered an objective function taking into account the deviations between calculated and experimental values of the upper critical solution temperature for the three binary systems. Using a classical quasi-Newton optimization procedure, a new set of the three a_{mn} -parameters was determined. The new a_{mn} -values are provided in table 3 (see bold a_{mn} -values).

These new a_{mn} -values were used for calculating the liquid-liquid Minimum Miscibility Temperatures of the three binary systems. Results are given in table 4. In order to see the improvement brought by the modified UNIFAC-model, values of MMT predicted with the original version of the UNIFAC-model are also provided. Changing the three a_{mn} -parameters allows to notably increase the accuracy of the model.

The new set of a_{mn} -parameters can now be used to trustfully predict some minimum miscibility temperatures of ethanol + gasoil + water mixtures of industrial interest.

INFLUENCE OF THE GASOIL COMPOSITION ON THE MMT VALUE

In this study, four commercial gasoils (GO1, GO2, GO3 and GO4), the compositions of which are given in table 5 were selected. Such fossil fractions were considered because they contain different amounts of paraffinic, aromatic, naphthenic and sulfur compounds. It is thus possible to evaluate how the proportion of components issued from these chemical families modifies the value of the calculated minimum miscibility temperature when gasoils are mixed with anhydrous ethanol. As shown in table 5, the first gasoil (GO1) contains 84 % of aromatic compounds, 16 % of paraffinic compounds and no sulfur compounds. GO2 is more of less similar but contains 7.5 % of sulfur compounds. On the contrary, GO3 and GO4 contain large amounts of paraffinic compounds (more than 80 %), and small quantities of aromatics. GO4 has the particularity to contain a small amount of naphthenic hydrocarbons.

Our first task was thus to use the UNIFAC model to calculate the liquid-liquid phase diagram when anhydrous ethanol is added in each gasoil. The highest temperature at which a phase split occurs i.e. the MMT has also been calculated. The corresponding phase diagrams can be seen in figure 1 and the corresponding MMT are given in table 6.

By comparing the MMT values obtained for GO1 (84 % of aromatics + 16 % of paraffins) and GO3 (17 % of aromatics + 83 % of paraffins), it is clear that the MMT decreases when the aromatic content increases and that the MMT increases with the paraffinic content. In a similar way, by comparing the MMT values obtained for GO1 and GO2 (quite similar to GO1 but with 7.5 % of sulfur compounds), it is clear that the MMT strongly decreases when the sulfur content increases. GO4 contains a small amount of naphthenic compounds and has the highest MMT.

Components	GO1	GO2	GO3	GO4
1,4-dimethyl benzene (para-xylene)	1.0	1.0	0.9	0.7
1-ethyl-3-methyl benzene	2.6	3.0	4.2	1.9
1,2,3-trimethyl benzene	2.4	2.5	5.9	2.7
benzocyclopentane (indane)	0.7	0.6		
1-methyl-1-propyl benzene	0.7	0.6	1.2	
4-ethyl-1,2-dimethyl benzene	3.3	3.7	1.7	0.8
1,2,4,5-tetramethyl benzene	0.7	0.6		
1-methyl-4-(2-propenyl) benzene	2.0	2.0		
1-methyl-1-butyl Benzene	1.1	0.5		
Naphthalene	1.2	1.3	1.5	
2,3-dihydro-1,2-dimethyl 1H-indene	3.3	3.4		1.6
1-methyl naphthalene	7.0	8.6		
1-ethyl naphthalene		2.9		
1,2-dimethyl naphthalene	17.6	18.4		
1,4-dihydro-1,4-methano naphthalene	1.0	1.4		
1,3,6-trimethyl naphthalene	15.7			
n-pentadecane	1.0	2.1	4.78	7.3
fluorene	1.0			
1-methyl-1-ethyl naphthalene	0.9	17.2		0.8
2-methyl biphenyle	1.8	3.1		
n-hexadecane	1.4	2.2	3.3	6.5
7-ethyl-1,4-diethyl azulene	2.8	1.9		
2,2-dimethyl biphenyle	4.6	4.1		
n-heptadecane	2.0	1.1		4.0
phenanthrene	2.9	1.2		
n-octadecane	2.2	0.8	2.1	4.65
1-methyl phenanthrene	7.9	1.7		
n-nonadecane	2.3	0.7	1.3	3.2
9,10-dimethyl anthracene	1.4		1.1	
n-eicosane	2.2	0.7	0.8	3.6
n-heneicosane	2.1	0.6	0.6	3.2
n-docosane	1.8	0.6	0.5	1.3
n-tricosane	0.9	0.5	0.4	0.9
n-tetracosane	0.5	0.4		0.9
2,3-dihydro-1-methyl indene		0.6		
para-diisopropyl benzene		0.5		
n-pentacosane		0.3	0.3	
n-octane			6.25	
n-nonane			16.6	13.8
n-decane			8.5	4.85
n-undecane			17.6	7.35
n-dodecane				9.8
n-tridecane			1 - 0 -	8.6
n-tetradecane			17.35	9.85
n-hexacosane			0.3	
n-heptacosane			0.3	0.6
1-methylethyl cyclohexane				0.6
octyl cyclohexane				0.6
decyl cyclonexane		0.5		0.5
benzothiophene		0.5		
metnyl benzothiophene		0.9		
dimetnyi benzothiophene		3.0		
albenzo thiophene		0.9		
tnioxantnene	 0() =€41==€	1./		l

Table 5. Composition (mass %) of the four gasoils studied in this paper.

Gasoil	MMT (°C)
G01	48
GO2	9
GO3	78
GO4	100



Table 6. MMT values when anhydrous ethanol is mixed with different gasoils.

Figure 1. Liquid-liquid phase diagrams when ethanol is mixed with four different gasoils. Note: the MMT is the temperature corresponding to the maximum of the saturation curves.

We can thus suspect that the MMT increases with the naphthenic content.

INFLUENCE OF THE ETHANOL WATER CONTENT ON THE MMT VALUE

In a second step, instead of mixing anhydrous ethanol with each one of the four gasoils, it was decided to perform MMT calculations with industrial ethanol that is with ethanol containing water. In this section, the ethanol water content was varied between 1 and 10 % (mass percent). The corresponding MMT can be found in table 7 for the four gasoils studied. The corresponding curves can be seen in Figure 2. No experimental data are available for a possible comparison with values given in table 7. However, the parameters of the UNIFAC model used in this study were fitted on experimental data in order to predict with accuracy the MMT for binary systems containing representative components of gasoils. We thus can trust the calculations performed in this study.

Gasoil	Ethanol water content (mass %)	MMT (°C)
	1 %	35
	2 %	84
	3 %	140
GO1	4 %	196
	6%	311
	8%	440
	10 %	577
	1 %	2.0
	2 %	43.0
	3 %	89.0
GO2	4 %	126.0
	6%	247.0
	8%	353.0
	10 %	477.0
	1 %	45
	2 %	77
	3 %	120
GO3	4 %	162
	6%	241
	8%	320
	10 %	396
	1 %	67
	2 %	102
	3 %	141
GO4	4 %	181
	6%	264
	8%	342
	10 %	436

Table 7. Influence of the ethanol water content on the MMT values.

From table 7 and figure 2, it is clear that the water content in ethanol has a huge influence on the MMT value whatever the gasoil. As a general rule, the MMT expressed in kelvins is multiplied by two when the water content is varied from 1 to 10 %. This section thus emphasizes that it is particularly important to take into account the amount of water contained in the ethanol before performing a miscibility study.

CONCLUSION

Creating hybrid fossil/biogenic fuels by using ethanol as a gasoil extender is a challenging objective. Such additions are feasible as long as the gasoil and the ethanol are miscible. In order to be sure that, phase split will not occur whichever the ethanol content, it is necessary to mix the two fluids at a temperature higher than the minimum miscibility temperature (MMT). It is thus extremely important to know how this temperature is influenced by both the gasoil composition and the ethanol water content.

In this study, we have shown that:

- → the MMT increases with the paraffinic content and with the naphthenic content of the gasoil.
- → The MMT decreases with the aromatic content and with the sulfur content of the gasoil.
- ➔ The MMT sharply increases with the ethanol water content. Addition of 10 % by mass of water in the ethanol multiplies by two the MMT value.
- ➔ In presence of hydrated ethanol grades, it is essential to access to the MMT data either by experience or through a suitable predictive method which has been the matter of this paper.



Figure 2. Liquid-liquid phase diagrams when industrial ethanol (i.e. ethanol containing water) is mixed with four different gasoils. The ethanol mass water contents are : 1 %, 2 %, 3 %, 4 %, 6 %, 8 %, 10 %.

NOMENCLATURE

- G_i: occurrence of group i in the molecule.
- GO: gasoil
- MMT: minimum miscibility temperature.
- NGS: total number of groups defined by the UNIFAC method.
- q_i: molecular surface area of molecule i.
- Q_k: contribution of group k in the q-property.
- r_i: molecular Van der Waals volume of molecule i.
- R_k: contribution of group k in the r-property.
- x_i: mole fraction of component i
- z: coordination number
- γ_i : activity coefficient of component i.
- γ_i^{comb} : combinatorial part of the activity coefficient.
- γ_i^{res} : residual part of the activity coefficient.

 $v_k^{(i)}$: occurrence of group k in molecule i.

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