

ON THE APPLICATION OF SOLUTION OF GROUP THEORY TO DILUTE MIXTURES OF ISOMERS

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ABSTRACT

One of the limitations of any group contribution method developed so far is the impossibility to distinguish among different isomers. This paper suggests a very simple procedure to extend the solution of group theory to mixtures containing isomers. The procedure suggested is based on theoretical considerations and is derived from phase equilibrium data for mixture of isomers in the dilute regions. A linear correlation is found between the surface area fraction (q) of the molecules and the ratio of the critical pressure over the critical temperature. Furthermore the investigation shows that the q values of the organic compounds which exhibit strong association phenomena should be substantially reduced: numerical values are reported depending upon the availability of experimental data.

INTRODUCTION

In this paper we consider the UNIFAC group contribution model (Fredenslund et al. 1977) as representative of the different models developed so far based on the solution of group theory for calculating activity coefficients. This model suffers from a severe limitation when it is applied to phase equilibrium calculation of mixtures of isomers.

The UNIFAC model, like all the group contribution models based on the local composition concept, is made up from two contributions: a

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combinatorial part and a residual part. Aim of this study is to investigate the solution of group theory in the dilute region in order to extend the UNIFAC method for treating isomers and improve the performance of the method in the dilute region. The structure and the group interaction parameter matrix of the original UNIFAC method are maintained as they were published. Consequently all the conclusion we will get on the combinatorial parameters can be applied directly to the original equation: the same computer programs with the same parameter files can then be used. The investigation is carried out in the dilute region since the expressions are simpler and allow direct connection between structural parameters and experimental data.

THEORY

The starting point of our investigation is the expression for the activity coefficients at infinite dilution according to the UNIFAC model:

$$\ln \gamma^{-1} = (\ln r_1/r_2 + 1 - r_1/r_2) + \ln \gamma^{-stv} + \ln \gamma^{-**} \quad (1)$$

$$\ln \gamma^{-**} = \sum_k n_k (\ln \Gamma_k - \ln \Gamma_k^*) \quad (2)$$

We will consider throughout this paper component 1 as a paraffin and component 2 as an organic compound.

Two different cases may arise when applying expression 1 and 2 to the dilute region, depending upon the component which is infinitely diluted.

Organic compounds in paraffins

Let us consider the case of a binary mixture made up of an organic compound (2) infinitely diluted in different paraffins (1). Expression 1 becomes the following:

$$\ln \gamma^{-2} = (\ln r_2/r_1 + 1 - r_2/r_1) + \ln \gamma^{-stv} + q_2(1 - \ln \varnothing_{12} - \varnothing_{21}) \quad (3)$$

where \varnothing_{12} are the interaction parameters between the solute and the alkanes groups. Equation 3 is rigorously valid only if the organic compound is a monogroup molecule such as water, methanol, acetonitrile and so on (see next paragraph for the expressions of the general case). For a given solute equation 3 shows clearly that the residual term remains the same for any paraffin considered since it is a function of the group interaction parameters which are constant. Changes are allowed only in the combinatorial term which, if we disregard the Guggenheim-Staverman contribution (numerically unimportant and leading sometimes to unreasonable results (Larsen, 1986)), reflects changes in the ratio of the volumes r_1 / r_2 .

TABLE 1
Experimental data of $\ln \gamma^\infty$ for paraffins (1) and water (2) at 298.15 K
($\ln \gamma^{\infty,0}$ is the combinatorial contribution). Data are from Sorensen
and Arlt, 1984 and Tiegs et al, 1986.

Paraffin (1)	r_1	$\ln \gamma^{\infty,1}$	$\ln \gamma^{\infty,2}$	$\ln \gamma^{\infty,0}$
n - hexane	4.4998	8.28	3.18	-.82
2 methyl pentane	4.4990	8.11	3.14	-1.01
3 methyl pentane	4.4990	7.89	3.10	-1.02
n - heptane	5.1742	9.90	3.12	-1.01
3 methyl hexane	5.1734	9.32	2.98	-1.01
2,4 dimethyl pentane	5.1726	9.22	3.10	-.82
n - octane	5.8486	11.41	2.99	-1.19
2,4 dimethyl hexane	5.8470		2.43	-1.01
2,2,4 trimethyl pentane	5.8470	10.26	2.46	-1.19
2,3,4 trimethyl pentane	5.8463	10.22	2.41	-1.19
n - hexadecane	11.2438		2.69	
7,8 dimethyl tetradecane	11.2422		2.44	

Table 1 reports some experimental values of the activity coefficients at infinite dilution for water in different n - paraffins and iso - paraffins: there is an effect of branching in the value of $\ln \gamma^\infty$ and this effect is not taken into account by the almost negligible changes in the r values of the iso - paraffin with respect to the n - paraffin if calculated following Bondi (1968).

It is interesting to calculate the value of r_1/r_2 directly from the experimental data of $\ln \gamma^{\infty,2}$. If we use the Bondi's values for r and q of the organic compound and the interaction parameter matrix from the modified UNIFAC method, equation 3 contains only unknown r_1 . Since the residual term in eq 3 does not change with branching, we consider the difference between $\ln \gamma^{\infty,2}$ of the iso and the normal paraffin: the residual contribution vanishes and the ratio r_{iso}/r_n is directly obtained.

If $\ln \gamma^{\infty,2}$ is plotted versus the ratio r_{iso}/r_n as it is shown in figure 1, we can conclude that r_{iso}/r_n values are sensitive to branching. Even though in some cases the experimental uncertainty hides this effect a general trend of increasing the r_{iso}/r_n with branching is observed. This conclusion allows us to calculate directly from the $\ln \gamma^{\infty,2}$ the r values for an iso - paraffin, if we fix the r value of the normal paraffin to the one calculated following Bondi. Unfortunately the number and the quality of the experimental data available do not permit to derive a general correlation for r_{iso}/r_n .

A further consideration can be obtained if we take eq 3 by its own, in other words we do not consider the difference between $\ln \gamma_{\infty}^{-2}$ in a normal and in an iso paraffin, but the absolute value of $\ln \gamma_{\infty}^{-2}$ in a paraffin (normal or iso). Equation 3 can be used now to calculate the q value of the organic compound which reproduces correctly the experimental data in the dilute region. The r values are calculated according to the previous conclusion, the combinatorial term is fixed, the Staverman contribution may not be considered, and the residual term is given by the q value of the organic compound multiplied to a term which is constant.

Figure 1: experimental values of γ_{∞}^{-2} versus r_{iso}/r_n for binary systems of water with different n and iso paraffins: (Δ) hexane; (\square) heptane; (\blacktriangle) octane; (\bullet) nonane; (\circ) hexadecane.

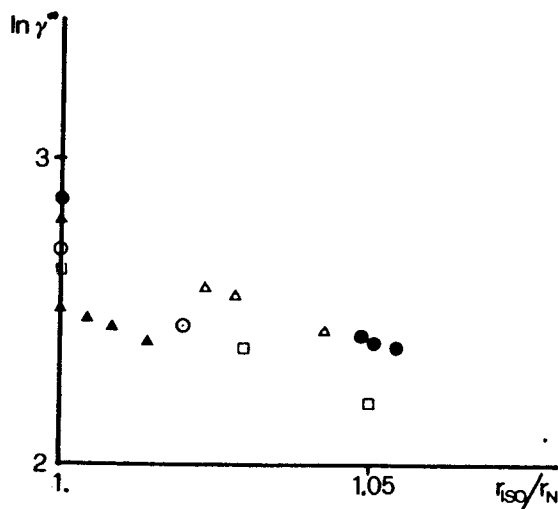


Table 2 shows the results obtained by using the modified UNIFAC method (Larsen 1986) with different organic compounds: it can be observed that in most cases a substantial reduction of q from Bondi's values is needed if we want to represent the data in the dilute region for binary mixtures of normal and iso - paraffins with organic compounds. The numbers reported in Table 2 are mean values obtained by fixing the organic group (or compound) and considering many different paraffins. This reduction is evident for the groups strongly associating such as water and alcohols: the contraction of the bond length with respect to that calculated following Bondi must be considered for representing the data in the infinite dilute regions, as it was suggested by Bondi himself. The methanol case is not an

exception because the Bondi value reported in table 2 is already reduced respect to the original one.

It is necessary to point out that the results of table 2 are valid only qualitatively since the parameter matrix used has been derived in connection with the Bondi's value. Consequently the numbers in table 2 cannot be used directly but have to be considered as a suggestion for the development of a new group contribution method.

TABLE 2
Structural q parameters calculated by the proposed method compared with the original from Bondi.

Group	Bondi's	This work
CH ₃ CN	1.724	1.872
CH ₃ OH	1.432	1.420
CH ₃ CO	1.488	.972
OH	1.200	.742
H ₂ O	1.400	.550
CH ₃ Cl	2.410	2.606

Paraffins in organic compounds

The results obtained in the previous section on the $r_{1\infty}/r_n$ can be used for determining the q values of iso - paraffins from the q value of the n - paraffins.

We consider now the case of paraffins (1) infinitely diluted in an organic compound (2); the UNIFAC expression for the infinite dilution activity coefficient is the following:

$$\ln \gamma^{-1} = (\ln r_1/r_2 + 1 - r_1/r_2) + \ln \gamma^{-1}_{STV} + q_1(1 - \ln \phi_{21} - \phi_{12}) \quad (4)$$

which is again valid only in the case of monogroup organic solvent (the general case is treated in the next paragraph).

We consider now a binary mixture of a n - paraffin infinitely diluted in an organic compound and a binary mixture of the relative iso - paraffin infinitely diluted in the same organic compound. The combinatorial term remains the same only if the Bondi's r values are used and the number of carbon atoms in the paraffin is the same. Nevertheless the last column of table 1, reporting the combinatorial contributions to the activity coefficients, shows that they are very small compared to the total value of γ^{-1} ; numerically speaking the combinatorial term can be considered constant even if the r ratio from the previous section is used.

The residual term is again the product of a constant term (in brackets) and the q which is now the q value of the paraffin.

Consequently this equation allows us to calculate the q value if the experimental value of the $\ln \gamma^{-1}$ is available. By simply considering table 1 one can see that the branching effect is rather important and the experimental values of the γ^{-1} are considerably different. Again this effect cannot be described by Bondi's q nor from the small variations in the r values in the combinatorial term.

Table 3 shows the results of the calculations: the numbers reported in the table are mean values obtained considering different organic solvents (alcohols, ketones, chlorocompounds). These values are compared with the original Bondi values and a general trend can be observed: the q values are decreasing as branching is increasing. On the contrary the values calculated from Bondi are almost constant and anyway their variations is not sufficient to reproduce the experimental reality.

Expressions for the general case

The investigation carried out so far was done considering binary mixtures of compounds defined as monogroup, namely compounds in which only one main interaction group was present such as paraffins, methanol, acetonitrile and so on. The results obtained are absolutely general and they do not depend upon the particular strategy of the group definition in the model. Accordingly, if we consider the expression of the infinite dilution activity coefficient of a generic organic compound infinitely diluted in a paraffin the expression is only more complicated, but the conclusions still hold. For a binary mixture the expression is the following:

$$\ln \gamma^{-2} = (\ln r_2/r_1 + 1 - r_2/r_1) + \ln \gamma^{-s_{xy}} + \ln \gamma^{-s} \quad (5)$$

$$\ln \gamma^{-s} = \sum_k n_k (\ln \Gamma_k - \ln \Gamma_k^1) \quad (6)$$

$$\ln \Gamma_k = Q_k [1 - \ln(\theta_k + \theta_j \varnothing_{kj}) - \theta_k / (\theta_k + \theta_j \varnothing_{jk}) - \theta_j \varnothing_{kj} / (\theta_j + \theta_k \varnothing_{kj})] \quad (7)$$

in which all the terms included in equation 7 are constant if the organic compound does not change. This is also the only assumption done in the monogroup case. The general case is only computationally more complicate but the conclusions are consistent with those obtained above. The same expressions and the same arguments hold also for the case of the paraffins infinitely diluted in organic compounds.

CORRELATION OF THE STRUCTURAL PARAMETER

The general trend observed for the q values with branching suggests the possibility of correlating the structural parameter q with molecular properties. The last column in table 3 shows the ratio of the critical temperature over the critical pressure for the paraffins considered. The trend of this quantity is the same as that of the q

values calculated directly from the experimental data: this suggest us a possible correlation of the q values with this ratio.

Figure 2: structural parameter q versus T_o/P_o for the Modified UNIFAC model: (\bullet) n - paraffins; (\circ) iso - paraffins; (Δ) Bondi.

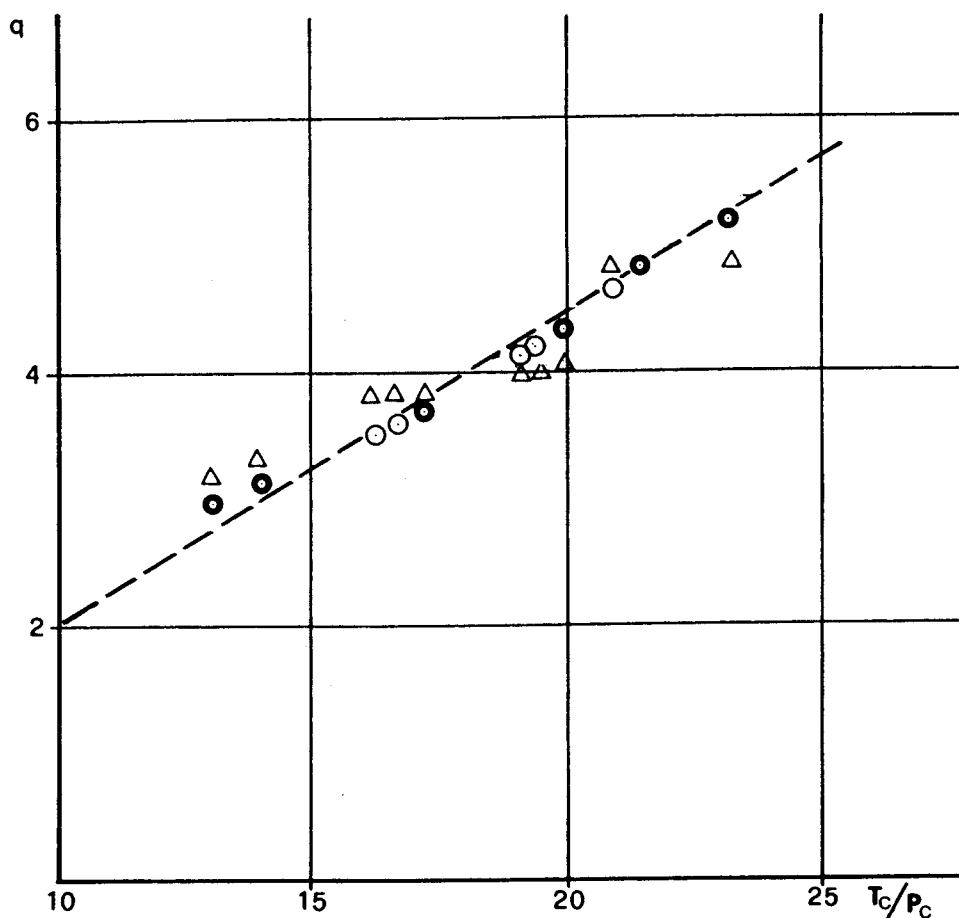


Figure 2 shows the q values calculated following this procedure by using the modified UNIFAC (Larsen, 1986) plotted versus T_o/P_o : the result is a straight line through the origin, while the q calculated from Bondi lies outside the straight line. The same conclusion is taken from figure 3 in the case of the original UNIFAC method. Consequently we suggest to calculate the value of q for an iso paraffin by simple linear extrapolation from the relative q value of the n paraffin calculated following Bondi: the extrapolation is done proportionally to the ratio T_o/P_o . The following expression may be used:

$$q = a + b T_c / P_c$$

(8)

where a and b are obtained from fig. 2 and 3.

TABLE 3
Structural q parameters for the normal and iso paraffins calculated by the proposed method.

Compound	q value calculated from			T_c/P_c
	H ₂ O	organic solvent	Bondi	
n - pentane	3.171	2.726	3.316	14.10
n - hexane	3.792	3.311	3.856	17.31
2 methyl pentane	3.759	3.268	3.852	16.76
3 methyl pentane	3.667	3.158	3.852	16.37
n - heptane	4.591	4.120	4.396	20.01
3 methyl hexane	4.350	3.828	4.392	19.25
2,4 dim. pentane	4.305	3.770	4.388	19.24
n - octane	5.306	4.836	4.936	23.22
2,3,4 trim. pentane	4.822	4.367	4.924	21.50
2,2,4 trim. pentane	4.805	4.351	5.008	21.05

CONCLUSIONS

A general correlation for the calculation of the q value of an iso paraffin has been developed from considerations based on the UNIFAC model written for dilute mixtures. The ratio of the r values is numerically unimportant and does not influence the conclusions on the q values. The q values are linearly depending upon the ratio of the critical temperature over the critical pressure which are normally available for most of the isomers of industrial importance. The parameter table of the UNIFAC or the modified UNIFAC are not changed by this procedure.

Figure 4 shows an example of application of the proposed method: the activity coefficients for the mixture iso octane - ethanol are predicted much better if the q value for the paraffin calculated from the ratio T_c/P_c is used. The q value of ethanol and the interaction parameters are taken from the original table of the modified UNIFAC method. It is not possible to use the ethanol q value from table 2 without recalculating the group interaction parameters.

The investigation has also shown that in order to reproduce the limiting activity coefficients for mixtures of paraffins and associating compounds it is necessary to consider smaller q values of the associating compounds.

The assumption of keeping constant the parameter matrix and the structure of the residual term leads to the consequence that the branching effect is taken into account by the combinatorial term, namely by the structural parameters r and q . We are aware that this approach can be dangerous especially in the very general case of isomers containing more than one functional group. However in this case it is necessary to consider the residual term and therefore the preferential interactions between the groups (Kehiaian, 1987): this topic is connected to the performance of group contribution models in predicting phase equilibria for mixture containing more than one functional group.

Figure 3: structural parameter q versus T_c/P_c for the UNIFAC model: (●) n - paraffins; (○) iso - paraffins; (△) Bondi.

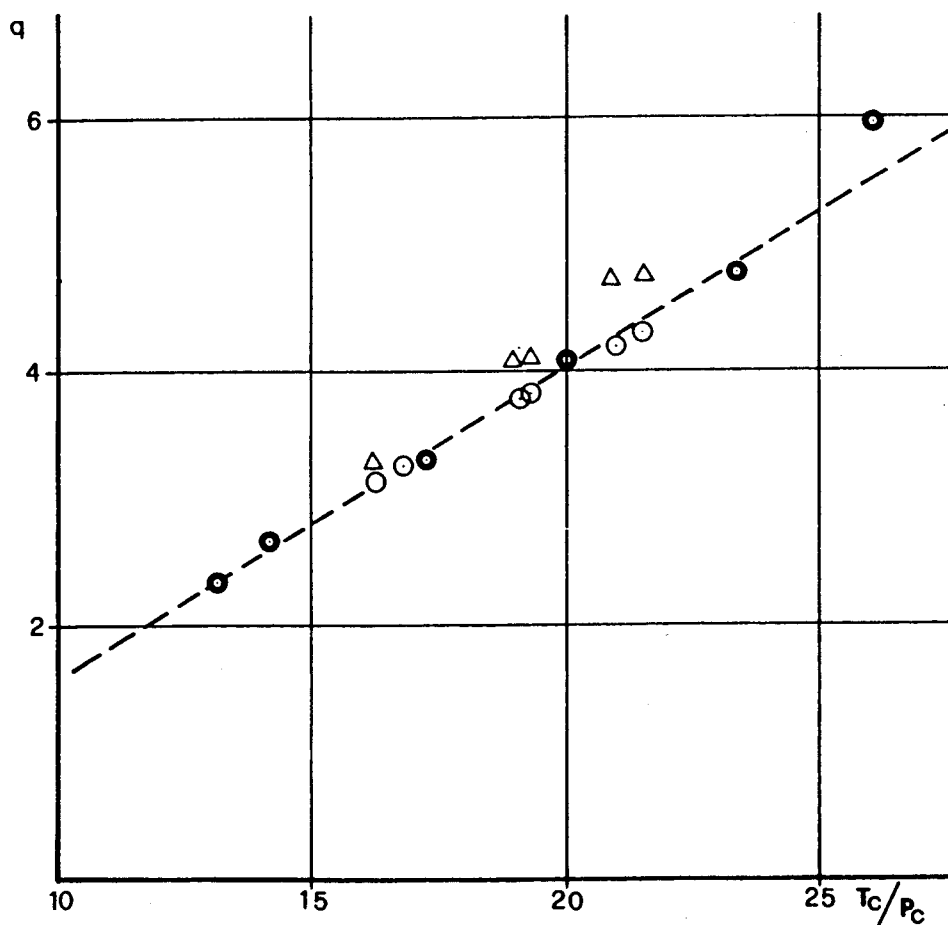
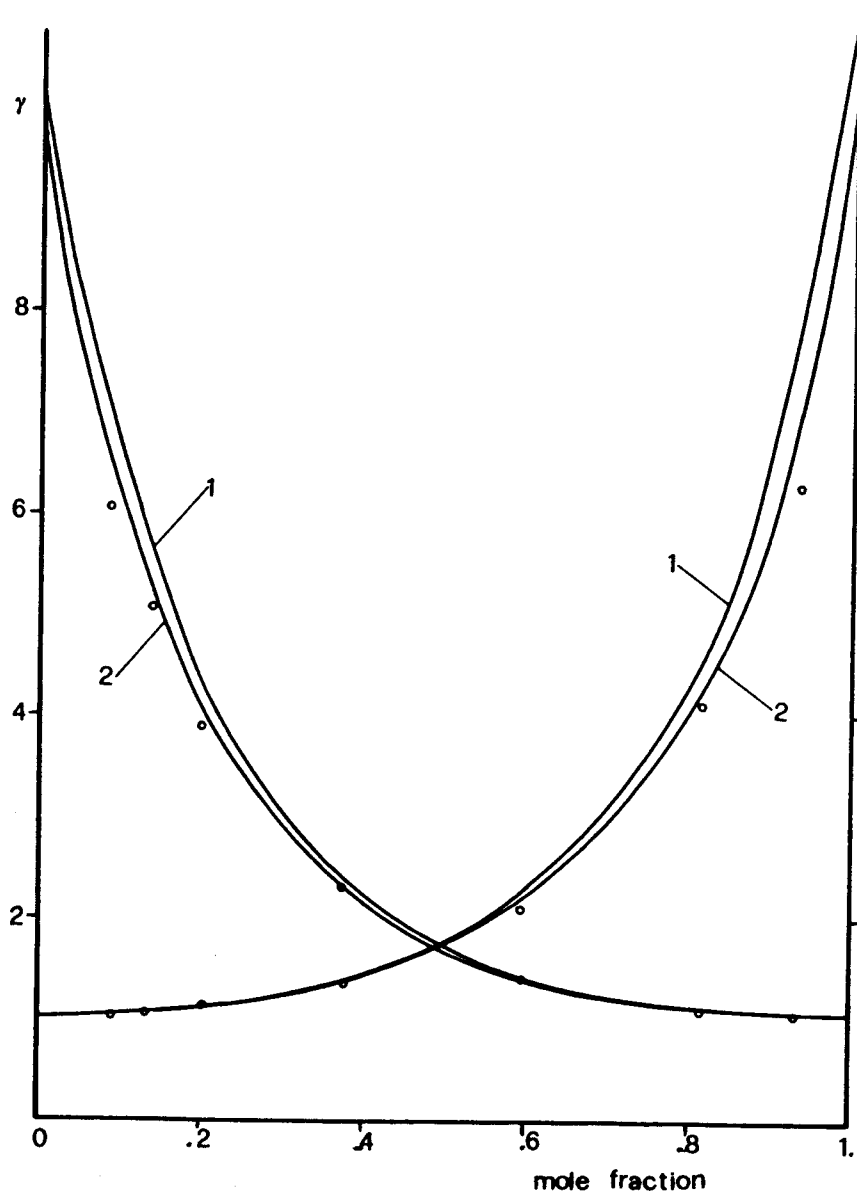


Figure 4: activity coefficients for the mixture ethanol - iso octane (2,2,4 trimethyl pentane) at 348 K: (1) Modified UNIFAC; (2) Modified UNIFAC with q calculated by the proposed procedure.



LIST OF SYMBOLS

a	coefficient expression 8
b	coefficient expression 8
P_c	critical pressure, [bar]
q	surface area fraction
r	volume fraction
T_c	critical temperature, [K]
γ	activity coefficient
Γ	group activity coefficient
ϕ	group interaction parameter
c	combinatorial term
res	residual term
ω	infinite dilution
iso	iso paraffin
n	normal paraffin
stv	Staverman - Guggenheim contribution

ACKNOWLEDGEMENTS

The authors thank MPI, Ministero della Pubblica Istruzione, for the financial support.

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