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Prediction of Solubility of Long-Chain Hydrocarbons in Various Solvents Using UNIFAC[1]

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The UNIFAC group contribution model has been widely used in the prediction of phase equilibria of various fluid mixtures. We have applied the method to predict the solubility of various long-chain hydrocarbon solids in a number of solvents of industrial importance. The calculated solubilities are compared with measured values and also with the predictions of the regular solution theory of Hildebrand and Scatchard. Some disagreements were found between the measured solubilities and the predicted values of both theories. Overall the UNIFAC scheme appears to be superior to the regular solution theory.

KEY WORDS: hydrocarbons; regular solution; solubility; solvents; UNIFAC.

1. INTRODUCTION

In an earlier paper Gmehling et al. [1] have shown how the equilibrium solubility of solids can be predicted using the UNIFAC group contribution model. UNIFAC has been used primarily to predict vapor–liquid and liquid–liquid equilibria properties of fluid mixtures. However, much less attention has been given to the prediction of solubilities of solids in pure components and mixed solvents. As pointed out by Gmehling et al. [1] this method can certainly be used in chemical process design involving solids and for preventing precipitation of a solid. In the chemical industry and also in various other applications there is often a need for selecting appropriate solvents to dissolve specific solids or fluids. This method is extremely useful in those applications.

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The UNIFAC method uses a group contribution concept and the activity coefficients of a solute–solvent system can be calculated where the group interaction parameters are known. For molecular species where minimal solubility data are available, this method is a very good approach to calculate activity coefficients and estimate corresponding solute solubilities as long as the group interaction parameters are determined by other means. Since UNIFAC is more quantitative than the traditional three-dimensional solubility parameter approach used to evaluate the solvency power of industrial solvents, it essentially competes with various other well-tried theories of solubility such as the regular solution theory of Hildebrand and Scatchard [2, 3]. The method has a slight advantage over regular solution theory in that it can predict both positive and negative deviation from ideality fairly easily.

In this work we revisit the problem of prediction of the solubility of solids via the UNIFAC solution of groups model, using selected hydrocarbons as test solutes. UNIFAC parameters developed for vapor–liquid equilibria are used in the prediction. Certain discrepancies in the comparison led us to reformulate the UNIFAC model, with the inclusion of a free volume term which was not included in the original formulation. The free volume term was obtained following Flory et al. [4, 5]. We have compared a fairly large number of reported data for mostly nonpolar and, in a few cases, slightly polar species to the calculated values obtained by our model and by the regular solution model of Hildebrand et al. [2, 3]. Some improvement in predictive accuracy was found with our model. We have also included 1, 1, 2-trichloro-1, 2, 2-trifluoroethane in our comparison and generated new group contribution terms for this chlorofluorocarbon.

2. THERMODYNAMIC FRAMEWORK

It has been shown by Prausnitz [6] that for a solution formed by heating the solute and solvent to the triple point, mixing them, and cooling the solution down to system temperature, the ratio of the fugacities can be written as

$$\ln\left(\frac{f_2^{S_0}}{f_2^{L}}\right)=\frac{\Delta H_f}{RT}\left(\frac{T}{T_M}-1\right)+\frac{\Delta C_p}{R}\left(\frac{T_M}{T}-1\right)-\frac{\Delta C_p}{R}\ln\left(\frac{T_M}{T}\right) \qquad (1)$$

$f_2^{S_0}$ and f_2^{L} are the fugacity of the solid and the liquid states, ΔH_f is the heat of fusion, T_M is the melting point of the system, T is the temperature of the system, and ΔC_p is the difference between the heat capacity of subcooled liquid and that of the solid $(C_p^l - C_p^S)$. This method neglects the heat of mixing effects and thereby limits the application to systems where the heat of mixing is not supposed to be very large.

Furthermore, we are going to neglect the term containing C_p because the required C_p data are not usually available, and in general the correction may be assumed to be small compared to the uncertainties in the activity coefficients.

Using Eq. (1) and neglecting the terms mentioned in the above paragraphs, the following expression is obtained.

$$\ln x_2 = -\ln \gamma_2 - \frac{\Delta H_f}{RT}\left(\frac{T}{T_M} - 1\right) \tag{2}$$

Here γ_2 is an implicit function of x and T, and therefore, an alternative method such as Newton's method or graphical method has to be used to solve this equation.

Solid enthalpies of fusion were obtained from Ref. 7. The activity coefficients of the solute in the solution can be determined using various methods. In this case we have used the regular solution theory [2, 3] and UNIFAC group contribution model [8] to determine the activity coefficients, which were then used to calculate the solubility following Eq. (2).

3. ACTIVITY COEFFICIENTS FROM VARIOUS MODELS

First, we describe in brief the activity coefficient expressions from the UNIFAC solution of groups model. Abrams and Prausnitz [9] used Guggenheim's quasi-chemical theory of liquid mixtures [10] and obtained a semitheoretical equation for excess Gibbs energy of liquid mixtures through the introduction of the local area fraction as the primary concentration variable. The resulting equation is called the universal quasi-chemical (UNIQUAC) equation and it uses only two adjustable parameters per binary. The effects of molecular size and shape are introduced through structural parameters obtained from pure-component data. The UNIFAC uses a group contribution concept with the UNIQUAC equation as the basis for calculating activity coefficients of molecules in a solution [8, 11]. The activity coefficient derived from UNIFAC is assumed to be made up of various functional groups in the molecule. Since the number of functional groups is lower than the number of actual molecules, the properties of a very large number of fluids and their mixtures are characterized by a lower number of parameters. Any group contribution method is approximate because the contribution of a given group in one molecule is not necessarily the same as that in another molecule, since the influence of any one group in a molecule may be affected by the nature of other groups within that molecule. The fundamental assumption of UNIFAC is group additivity, where the contribution made by one group is assumed to be independent of that made by another group. Despite all these assumptions the model still possesses sufficient goodness in predicting solubilities. In the following paragraphs the activity coefficient expressions are written down following Fredenslund et al. [8].

The activity coefficient in this model consists of two parts, the combinatorial contribution, due mostly to differences in molecular size and shape, and the residual contribution, arising mostly from differences in intermolecular forces of attraction. For a component in multicomponent solution the activity coefficient is given by

$$\ln \gamma_i = \ln \gamma_i^{\mathrm{C}} + \ln \gamma_i^{\mathrm{R}} \tag{3}$$

where

$$\ln \gamma_i^{\mathrm{C}} = \ln \frac{\phi_i}{x_i} + \frac{Z}{2} q_i \ln \frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i} \sum x_i l_i \tag{4}$$

and

$$l_i = \frac{Z}{2}(r_i - q_i) - (r_i - 1) \tag{5}$$

The coordination number Z is taken to be 10 following Abrams and Prausnitz [9]. The area fraction and the segment fraction are related to the mole fraction x_i by

$$\theta_i = \frac{q_i x_i}{\sum_j q_j x_j}, \qquad \phi_i = \frac{r_i x_i}{\sum r_j x_j} \tag{6}$$

Here pure-component parameters θ and ϕ are, respectively, measures of molecular volumes and molecular surface areas (Van der Waals), which are calculated using the method of Bondi [12]. These, in turn, are given by contributions due to various groups in the molecule

$$r_i = \sum_k v_k^{(i)} R_k, \qquad q_i = \sum_k v_k^{(i)} Q_k \tag{7}$$

where $v_k^{(i)}$, always an integer, is the number of groups of type k in molecule i. Group contributions to area and volume parameters R_k and Q_k are given by Fredenslund et al. [8, 14]. The residual contribution to activity coefficient γ_i^R is given by

$$\ln \gamma_i^R = \sum_k v_k^{(i)} [\ln \Gamma_k - \ln \Gamma_k^{(i)}] \tag{8}$$

Here $k = 1,\ldots, N$, where N is the number of different groups in the mixture, Γ_k is the residual activity coefficient of group k in a solution, and $\Gamma_k^{(i)}$ is the residual activity coefficient of group k in a reference solution containing only molecules of type i. $\Gamma_k^{(i)}$ is necessary to obtain the normalization condition, where the activity coefficient becomes unity as $x \rightarrow 1$.

The group residual activity coefficient is related to the composition and temperature through

$$\ln \Gamma_k = Q_k \left[1 - \ln \left(\sum_m \theta_m \psi_{mk} \right) - \sum_m \left(\frac{\theta_m \psi_{km}}{\sum_n \theta_n \psi_{kn}} \right) \right] \tag{9}$$

m and n run through indices 1 through N, the number of groups. This equation also holds for $\Gamma_k^{(i)}$. Here θ_m and ξ_m are given by

$$\theta_m = \frac{Q_m \xi_m}{\sum Q_m \xi_m}, \qquad \xi_m = \frac{\sum \nu_m^{(j)} x_j}{\sum_j \sum_n \nu_n^{(j)} x_j} \tag{10}$$

j runs through indices 1 through M, the number of components, and n runs through indices 1 through N, the number of groups.

In Eq. (9) the interaction parameter ψ_{nm} is given by

$$\psi_{nm} = \exp(-a_{nm/T}) \tag{11}$$

and a_{nm} is actually given by

$$a_{nm} = U_{mn} - U_{nm} \tag{12}$$

The U_{mn}'s are the measures of interaction between group m and group n. Fredenslund and his co-workers have correlated a large number of VLE data and compiled the group interaction parameters [8, 11, 13, 14].

Although UNIFAC has been applied to a large class of molecules, mostly small in size, with a great deal of success [8], our initial attempt to apply this scheme to long-chain molecules met with some disagreement. The theory does not account for the free volume of molecules; it essentially considers the solution an assembly of closely packed molecules, which is not physically true for longer-chain molecules. Flory and his co-workers [4, 5] have done extensive work on long-chain hydrocarbon liquids, where they developed a theory to predict the activity coefficient of liquid mixtures of n-alkanes with a reasonable degree of accuracy. However, their theory is not entirely predictable because it contains binary interaction parameters. In our formulation we have included the essentials of Flory's approach by keeping his free volume term, which contributes to the combinatorial part, and we have used UNIFAC to calculate the interaction part. We write the activity coefficient of the mixture in the following way:

$$\ln \gamma = \ln \gamma_{\mathrm{UNIFAC}} + \ln \gamma_{\mathrm{FV}} \tag{13}$$

γ_{FV} is the free volume part which follows from Flory's derivation of the activity [4, 5] and used by Oishi and Prausnitz [15],

$$\ln a_i^{\mathrm{FV}} = 3C_i \ln \left[\frac{\tilde{V}_i^{\frac{1}{3}} - 1}{\tilde{V}_{\mathrm{M}}^{\frac{1}{3}} - 1} \right] - C_i \left[\frac{\tilde{V}_i}{\tilde{V}_{\mathrm{M}}} - 1 \right] \Big/ \left[1 - \frac{1}{\tilde{V}_i^{\frac{1}{3}}} \right] \tag{14}$$

and γ_i^{FV} is related to a_i^{FV} in the usual way:

$$\gamma_i^{\mathrm{FV}} = a_i^{\mathrm{FV}} / x_i \tag{15}$$

C_i is, in general, a function of the equation of state parameters and, in this case, specifically that of the solute. $\tilde{V}_i$, the reduced volume, is the ratio of molar volume to characteristic volume V_i^* used by Flory [4, 5] in his equation of state. $\tilde{V}_{\mathrm{M}}$ is the mole-fraction average of the reduced volume. In this case we have used the hard-core estimate of the characteristic volume

$$V_i^* = \alpha_i r_i \tag{16}$$

where α_i is a constant and r_i is the group surface area of the molecule calculated following Bondi [12].

The expression for the activity coefficient for a regular solution following Hildebrand et al. [2], including the effects due to molecules of dissimilar sizes, is as follows:

$$\begin{aligned} RT \ln \gamma_1 &= V_1^{\mathrm{L}} \tilde{\theta}_2^2 (\delta_1 - \delta_2)^2 + \ln \tilde{\theta}_2 + \ln \tilde{\theta}_1 (1 - V_2^{\mathrm{L}} / V_1^{\mathrm{L}}) \\ RT \ln \gamma_2 &= V_2^{\mathrm{L}} \tilde{\theta}_1^2 (\delta_1 - \delta_2)^2 + \ln \tilde{\theta}_1 + \ln \tilde{\theta}_2 (1 - V_1^{\mathrm{L}} / V_2^{\mathrm{L}}) \end{aligned} \tag{17}$$

Here again, γ's are the activity coefficients, δ's are the solubility parameters, $\tilde{\theta}$'s are the molar averages of volume, and V^{L}'s are the liquid molar volumes. The subscripts 1 and 2 stand for components 1 and 2. A comprehensive collection of δ's and V^{L}'s can be found in Ref. 17.

4. RESULTS AND DISCUSSION

We have chosen a series of homologous hydrocarbons as our solutes and compared the measured solubilities in a number of solvents to our calculated values using the methods described in the previous section. We have used *n*-hexadecane and *n*-heptadecane solubilities measured by Ralston et al. [18], some recently measured octadecane solubilities by Chang et al. [19], and *n*-dotriacontane solubilities measured by Ralston et al. [18], Chang et al. [19], and Hildebrand et al. [20] and also measured in our laboratory. The measurements encompass nonpolar and slightly polar solvents which include *n*-heptane, CCl_4, chloroform, 1, 1, 2-trichloro-1, 2, 2-trifluoroethane(FC-113), benzene, and cyclopentane. We have also compared our calculated values with solubility data on naphthalene in various polar and nonpolar solvents. These data were also measured over a temperature range which enabled us to compare the temperature dependence of the theories.

The group interaction parameters for a number of the groups in these solute–solvent systems were obtained from Fredenslund et al. [9, 14, 21]. Since very few interaction parameters were available for chlorofluorocarbons, these were obtained at our research laboratory. This enabled us to extend the UNIFAC method to a few chlorofluorocarbon-containing solvents and solvent mixtures. The solubility of *n*-dotriacontane and naphthalene in solvents was measured by gravimetric titration. Weighed amounts of the solutes were introduced in a test tube (screw-on cap). Solvent was gradually added to the test tube and stirred continuously in a thermostated bath with the temperature kept at 25 ± 0.2°C. To avoid overshooting titration was stopped when a piece of single crystal was found left in the solution after continuous stirring for 24 h. Solvent was added at very small increments, and the solution stirred continuously until this crystal disappeared.

This was repeated several times and the solution was weighed carefully to determine the weight percent of the solute in the solution. The screw-on cap assures no loss of solvent during the experiment. The reproducibility of the solubility was found to be within ±0.1% and we estimate an overall accuracy of ±0.2% in the final values. *N*-Dotriacontane was obtained from Wiley Organics and naphthalene was obtained from Fisher Scientific, with a purity of 99+%. Our solubility measurements agreed within the experimental error of literature values [20, 21, 22] where such data were available.

Table I shows a comparison of solubility data on *n*-heptadecane, *n*-hexadecane, *n*-octadecane, and *n*-dotriacontane measured by various authors in a number of solvents over a range of temperatures. The results for *n*-heptadecane, *n*-hexadecane, and *n*-octadecane solubilities in nonpolar and slightly polar solvents show that UNIFAC predictions are comparable to regular solution calculations and a large fraction of the error may be coming from regions where the solubility of the solids is too low in general, being far from the melting point of the substances. As expected the free

Table I. Comparison of Measured and Calculated Solubility Data

System	Temp. range (°C)	Absolute deviation $\left[\frac{(X_{\mathrm{exp}}-X_{\mathrm{calc}})}{X_{\mathrm{exp}}}\right]$ (%) UNIFAC	UNIFAC + FV	Reg. sol.
n-Hexadecane/CCl_4	−20–15	21.1	19.3	20.0
n-Heptadecane/CCl_4	−10–15	11.8	11.6	8.6
n-Dotriacontane/CCl_4	20–60	38.8	12.5	66.4
n-Hexadecane/$CHCl_3$	−20–15	26.0	24.7	4.2
n-Heptadecane/$CHCl_3$	−10–15	20.2	19.2	3.8
n-Dotriacontane/$CHCl_3$	20–60	35.0	18.1	47.1
n-Hexadecane/cyclohexane	10–15	4.6	4.6	8.2
n-Heptadecane/cyclohexane	10–15	3.0	1.0	3.4
n-Dotriacontane/cyclohexane	30–60	23.0	9.0	Very large
n-Octadecane/*n*-heptane	21–39	15.2	2.5	13.2
n-Dotriacontane/*n*-heptane	29–61	65.0	21.0	42.0
n-Dotriacontane/benzene	24–52	54.0	22.0	71.2

volume correction makes a slight improvement in the comparison with experimental data, but not as much as hoped for.

For *n*-dotriacontane, where the size of the molecule is much larger compared to the other hydrocarbons, we see a significant change in the agreement between the experimental and the calculated values. In these calculations we have chosen the value of C_1 in Eq. (14) to be 5.0 and found this to be almost a universal constant for the C_{16}–C_{32} series of hydrocarbons as expected from Flory's results on similar systems [4, 5]. The other constant in Eq. (16) was also found to be nearly constant, $\simeq 19.14$. This value agrees reasonably well with Flory's value ($\simeq 14$–15). In Table II we

Table II. Solubility of *n*-Dotriacontane in a Few Solvents at 298.15 K

Solvent	Exp. obs.[a] Wt %	Mol %	Calculated values (Mol %) UNIFAC	UNIFAC + FV	Reg. sol.	Ideal
FC-113	0.25	0.10	0.34	0.06	0.07	0.21
Dichloromethane	0.55	0.11	0.72	0.32	0.03	0.21
Cyclopentane	10.2	1.74	3.38	2.21	0.17	0.21
Genesolv® DMC	0.88	0.21	2.57	0.40	0.17	0.21

[a] This laboratory.

Table III. Solubility of Naphthalene in Various Solvents

		Mol % Naphthalene			
Solvent	Temp. (°C)	Exp. obs.	UNIFAC	Reg. sol.	Ideal
Hexane	40	22.2	26.75	40.0	44.0
Acetone	40	37.8	35.8	44.0	44.0
	25	20.0	20.1	20.0	30.6
MeOH	40	4.12	4.83	25.4	44.0
	25	2.3	2.9	20.3	80.6
Heptane	20	10.14	14.1	26.1	26.9
	25	11.31	16.6	29.5	30.6
	30	13.19	19.15	33.0	34.7
	40	18.48	26.9	40.7	44.0
FC-113	25	8.5	12.3	28.8	30.6
Dichloromethane	25	25.9	34.7	30.6	30.6
Cyclopentane	25	17.8	21.6	30.0	30.6
Genesolv DMC	25	29.7	33.3	29.9	30.6

have compared calculated vs measured solubilities of dotriacontane in 1, 1, 1-trichloro-1, 1, 1-trifluoroethane, dichloromethane, cyclopentane, and a proprietory commercial azeotropic solvent containing these three components called Genesol® DMC. These measurements at 25°C were done in our laboratory. The comparison again shows remarkable improvements when free volume corrections are added to it. However, the calculated solubilities from UNIFAC are comparable or slightly inferior to those calculated by regular solution theory except in the case of cyclopentane.

We also found that calculations from UNIFAC agree much better with measured solubilities for naphthalene than for long-chain hydrocarbon solutes. In this case the free volume correction is found to have a negligibly small effect on the naphthalene solubility.

In Tables I–III we have also included comparisons of measured values to regular solution theory predictions. We have found that over the temperature range studied, regular solution theory agrees comparably with UNIFAC predictions except for *n*-dotriacontane. The observed discrepancy is far too large. For regular solution theory another problem existed in estimating the solubility parameters for these long-chain hydrocarbons, and a group contribution method from Barton [17] has been used. For naphthalene, however, UNIFAC alone was found to be clearly superior to regular solution theory predictions. Data from Refs. 22 and 23 and our own measurements (all 25°C data in Table III) were used for comparison.

Genesolv is a registered trademark of Allied Corporation.

For regular solution calculations the temperature dependence of the solubility parameters was calculated using Watson's form given in Ref. 17.

In analyzing predicted dotriacontane solubilities the transition from a nonrotating to a rotating phase as indicated by Hildebrand et al. [20] could not be accounted for in a comprehensive manner. A recent DSC measurement by Chang et al. [19] confirms this behavior, where they have found a transition occurring at 338.9 K with a heat of transition of 42.7 $\mathrm{kJ \cdot mol^{-1}}$ and a melting point at 342.1 K with a heat of fusion of 76.0 $\mathrm{kJ \cdot mol^{-1}}$. This information can be utilized to modify Eq. (5), where the simple heat of fusion term can be replaced by a term of the form,

$$\frac{\Delta H_{\mathrm{f}}}{R}\left(\frac{1}{T_{\mathrm{M}}}-\frac{1}{T_{\mathrm{tr}}}\right)+\frac{(\Delta H_{\mathrm{f}}+\Delta H_{\mathrm{tr}})}{R}\left(\frac{1}{T_{\mathrm{tr}}}-\frac{1}{T}\right) \tag{18}$$

The addition of this term accounts for a small part of the difference found but it is by no means sufficient to improve the agreement between the values calculated using Eq. (2) and the measured values.

The omission of the specific heat term in a similar way was expected to account for some of the discrepancies found between the observed and the calculated solubilities. Reliable specific heat measurements were not available, and again an order of magnitude estimate shows that the large discrepancy cannot be accounted for by this correction. The two terms containing the specific heat in Eq. (1) are of the same order of magnitude but of opposite sign and they do tend to cancel each other.

Our results, however, do show that for a long-chain molecule such as *n*-dotriacontane, the inclusion of a free volume term significantly improves the agreement between calculated and measured values.

5. CONCLUSION

We have tried to establish the usefulness of the UNIFAC solution of groups concept to solubility calculations, primarily linear-chain hydrocarbon solids in various solvents. We have also compared the solubility of naphthalene in various solvents to our calculations. UNIFAC has been well studied for solutions of a large class of relatively smaller molecules, especially for their VLE properties, with a reasonable degree of success [8]. However, it has not been widely used to calculate the solubility of solids in various solvents. Our calculations indicated that for nonpolar and slightly polar solvents, it worked reasonably well for long-chain hydrocarbon solids with chain lengths of between 16 and 18 carbon atoms and it gives solubility values comparable to regular solution theory calculations.

However, for higher chain lengths such as *n*-dotriacontane ($C_{32}H_{66}$), both conventional UNIFAC and regular solution theory did not do quite so well in predicting its solubility in a number of nonpolar and slightly polar solvents. The discrepancy is sufficiently large as shown in Tables I and II, and it cannot be explained by the use of the simple volume correction [Eq. (17)], the use of the additional specific heat term given in Eq. (1), or the use of the heat of transition effect given in Eq. (18).

Therefore, we reformulated the activity coefficient expression with an additional free volume correction suggested by Flory and his co-workers [4, 5] for linear-chain molecules. This free volume correction was not properly accounted for in UNIFAC. The UNIFAC approach assumes a close-packed structure of the solution. Flory's free volume correction contained two adjustable parameters, the constant C_i and the characteristic volume of the molecule V^*, shown in Eq. (14). In our study of linear-chain hydrocarbons in various solvents we used two parameters, C_i and α_i [given by Eq. (16)], as adjustable constants.

The resulting calculations showed that the agreement between the experimental and the calculated values improved by orders of magnitude with this additional term. Furthermore, for the linear-chain molecules studied C_i and α_i seemed to be parameters dependent on the solute and are found to be almost universal constants. The values of these constants are also of the same order of magnitude found by Flory in his work on mutual solubility of paraffins [4, 5]. In the present work we have used an optimum value of $C_i = 5.0$ [Eq. (14)] and $\alpha_i = 19.42$ [Eq. (16)] for all of these linear-chain molecules. Whether these constants are universal for even longer-chain molecules is an open question and further experimental work needs to be done to prove this point.

We have extended the range of applicability of the UNIFAC method to include long-chain molecules. The major advantage of this formulation over methods due to Flory [4, 5] lies in the fact that we could use the UNIFAC approach to account for the interaction part, and therefore, we do not need all the individual binary interaction parameters needed in the work of Flory and his co-workers [4, 5]. UNIFAC also has the advantage of extending to highly nonideal solutions for which regular solution theory cannot be used. We feel that the method can be extended to polar and highly nonideal systems fairly easily.

We have also included limited solubility data on chlorofluorocarbons in our comparison. The solubility of *n*-dotriacontane in chlorofluorocarbon-containing solvents again showed that our modified UNIFAC formulation containing the free volume term could represent the data much better than UNIFAC alone.

Finally, we have carried out a comparison of naphthalene solubility in various solvents measured by various authors including measurements done in our own laboratory to calculations via UNIFAC. As expected the free volume effect is found to be much smaller for naphthalene. The solubility of naphthalene in chlorofluorocarbon-containing solvents compared very well to calculations using UNIFAC alone, without the free volume correction.

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