Ministry of
the Environment

National
Environmental
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Environmental Exposure Analysis of Chemicals

NERI Technical Report No. 69

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Ministry of the Environment
National Environmental Research Institute
January 1993

Data Sheet

Title:	Environmental Exposure Analysis of Chemicals
Author:	Fei Chen Fredenslund
Department:	Department of Policy Analysis
Serial title and No.:	NERI Technical Report No. 69
Publisher:	Ministry of the Environment National Environmental Research Institute
Year of publication:	January 1993
Layout:	Else Snitker
Drawings:	Fei Chen Fredenslund
Please quote:	Fredenslund, F. C. (1993): Environmental Exposure Analysis of Chemicals. National Environmental Research Institute. 96 pp. - NERI Technical Report No. 69 Reproduction permitted only when quoting is evident.
Terms:	physico-chemical properties, QSAR, emission, UNIFAC, exposure assessment, waste water treatment
ISBN:	87-7772-093-8
ISSN:	0905-815X
Paper quality:	Multicopy, 90 g
Printed by:	Grafisk Service, RISØ
Circulation:	200
Number of pages:	96
Price:	100 Dkr. (incl. 25% VAT, excl. freight)
For sale at:	National Environmental Research Institute Department of Policy Analysis Frederiksborgvej 399 P.O. Box 358 DK-4000 Roskilde Phone: +45 46 30 12 00 - Fax: +45 46 30 11 14

Preface

Environmental exposure assessment is one of the key elements in the context of environmental hazard and risk assessment. The objective of the exposure assessment is to identify the potential release of a substance into the environment under specified circumstances and to predict environmental concentrations, PEC, as a function of time and location.

Denmark is engaged in the environmental hazard and risk assessment work carried out within the chemicals programs of EEC and OECD. The objective of this project is to supply the scientific basis for this work. This project has been financed partly by the Danish Environmental Protection Agency and the National Environmental Research Institute.

The report first gives the discussion and implementation of QSAR approaches for estimation of physico-chemical properties which are of important for the environmental fate modelling. Then, a general view of the present status on environmental exposure assessment modelling and a detailed analysis for several existing models are presented.

The author wants to express her thanks to John Holten-Andersen and Henrik Tyle for their inspiring and encouraging discussions, and to Else Snitker for making the report ready for printing.

Abstract

Background

The UNIFAC group-contribution method is a well-known model parallel to QSARs (Quantitative Structure-Activity Relationships) *(Fredenslund et al., 1975, 1977)*. The latest UNIFAC group-interaction parameters have been used in this work to evaluate the applicability of the UNIFAC model for predicting environmentally important physico-chemical properties, among others 1-octanol/-water partition coefficients and water solubilities. It has been shown the UNIFAC model has a great potential for environmental applications, but also that some modifications are necessary.

Following the evaluation, a new set of UNIFAC group-interaction parameters has been developed on the basis of infinite dilution activity coefficients of organic compounds in water. Thus, for environmental purposes, the accuracy of the UNIFAC model has been enhanced specially for the systems containing some highly hydrophobic compounds which are of special interest in an eco-toxicological context.

Computerised models for environmental exposure analysis

For environmental exposure analysis a number of partly computerised models have been developed. For example, the OECD Environmental Monograph No. 27 "Compendium of environmental exposure assessment methods for chemicals" represents a good compilation of several exposure models used by various institutions for different purposes. However, the applicability of the models presented in the compendium varies a lot and is of course dependent on the availability of the data needed and on the purpose for which the models have been developed.

In this work, several exposure assessment models have been applied to twelve selected chemicals. Interesting and diverse results were obtained by applying these models. An analysis has been given for the obtained results.

Table validation

The removal rates of chemicals through a waste water treatment plant (WWTP) are needed for the prediction of initial environmental concentrations. In the EEC guidance of environmental risk assessment of new chemicals, a table *(RIVM report 718703001)* has been adopted to estimate the removal rates of chemicals according to certain key physico-chemical properties of these chemicals. The model, which was originally used for the construction of the table, was run on the selected chemicals attempting to validate the table. It was observed that the table is not reliable for the estimation of the fate for certain chemicals in a waste water treatment plant. More investigations should be carried out to modify the table.

1 Introduction

Definition

Environmental exposure assessment is an essential part in the context of environmental hazard and risk assessment. In the framework of environmental hazard assessment, the potential for a substance to be present in the environment is related to the effects of the substance on the ecosystem. One key element in this process is the establishment of so-called "PEC / NEC" ratios (Predicted Environmental Concentration / No Effect Concentration). For new chemicals the exposure can only be of predictive nature. The assessment involves estimation of the emission sources and emission rates of a substance, and the subsequent exposure pathways, based upon predictive models.

A similar approach can be established for existing substances. However, for these substances there might be monitoring data available, which could be used to validate the predictive concentrations.

Relevant data

The compounds specific data which are most important for environmental exposure assessment comprise vapor pressure, water solubility, 1-octanol/water partition coefficient, hydrolysis half life time, photolysis half life time, soil sorption coefficient, bioconcentration factor, and information on biodegradability.

Date required for exposure assessment are not always available. Missing data may be substituted by QSAR (Quantitative Structure-Activity Relationships) estimations *(Calamari and Vighi 1987, Turner et al. 1987, Karcher and Devillers 1990).*

2 QSAR development

---- New developments of the UNIFAC model for environmental application

2.1 Introduction

State of art

Relationships between the structure of a chemical and its chemical, physical and biological properties are becoming of increasing interest for application in environmental hazard assessment *(e.g. Sheehan et al. 1985, Karcher and Devillers 1990, Hermens and Opperhuizen 1991)*. Depending on which type of variable calculated, these methods use one or several structurally derived descriptors of a chemical to predict the activity, the partitioning, or other interactions with the environment. The application of QSARs for estimation of physico-chemical characteristics is generally simpler and more mature compared with that in the field of toxicology, the latter is of high complexity for possible interactions between the chemical and the receptors within organisms leading to toxic effects. A further complexity is the distribution and accumulation processes which to a large extent also have a great influence on the toxicological effects.

Necessarity

Physico-chemical properties play an important role in the environmental exposure assessment of chemicals. However, for most chemicals the physico-chemical properties that govern their distribution processes are not always available. Also, because of the large number of chemicals in active use *(EINECS, 1987)*, there is an incentive and growing need for some form of early screening methods for the estimation of physico-chemical properties of chemicals, so that timely action could be taken in evaluating their impact on the environment. In the cases where measured values cannot be obtained, use of QSARs offers a good alternative.

UNIFAC method

The UNIFAC group-contribution method is a well-known model parallel to QSARs *(Fredenslund et al. 1975, 1977)*. It was developed for chemical engineering purposes, has been widely applied in many areas of chemical engineering, and has been proven to be a fast and reliable tool for predicting liquid-phase activity coefficients. A revised UNIFAC group-interaction parameter table has been published recently *(Hansen et al. 1991)*. The revised parameters have improved the reliability of UNIFAC model and extended the range of applicability of the method. The objectives of this work are both to study and to modify the applicability of the UNIFAC model for calculation of physico-chemical properties for environmentally relevant chemicals.

2.2 Environmental applications of the UNIFAC model

2.2.1 Principles of the UNIFAC model

Principle

The UNIFAC model is based on the group-contribution concept. The basic idea of the group-contribution method is that compounds may be structurally decomposed into functional groups (for instance, all the linear alkanes contain only CH_3 and CH_2 groups), each having a unique contribution toward the compound property. The attractive aspect of this approach is that whereas there are thousands of chemical compounds of interest in commercial use, the number of functional groups which constitute these compounds is much smaller. Therefore, if we assume that a physical property of a fluid is the sum of contributions made by the molecules' functional groups, we obtain a possible technique to utilize existing experimental data for predicting the properties of systems for which no experimental data are available.

Fundamental equation

In the UNIFAC model, the activity coefficient γ_i is calculated from two parts:

$$\ln\gamma_i = \ln\gamma_i^C + \ln\gamma_i^R \qquad (1)$$

where γ_i is the activity coefficient for the component i, γ_i^C is the combinatorial part, and γ_i^R the residual part. The combinatorial term takes into account entropy effects and depends on the size and the shape of molecule i. In the combinatorial part, the group surface volume and area for each functional group are used as model parameters. These are determined using the compilation by *Bondi (1968)* and presented in Table M-1 of Appendix C as R_K and Q_K. The residual term is mainly governed by the energetic interactions of different groups of molecules. The group-interaction parameter, a_{mn} and a_{nm}, are introduced in this term. Reliable experimental binary vapor-liquid equilibrium data for representative systems are required to determine the group-interaction parameters.

Thermodynamic consistent data

There is a very important, so-called Gibbs-Duhem equation in thermodynamics. The Gibbs-Duhem equation interrelates activity coefficients of all components in a mixture. Therefore, if data are available for all of the activity coefficients, these data should obey the Gibbs-Duhem equation; if they do not, then the data cannot be correct. This lay the foundation of thermodynamic consistent test *(Christiansen and Fredenslund, 1975)*. All the vapor-liquid equilibrium data used to determine UNIFAC group-interaction parameters have passed the thermodynamic consistency test.

Availability

In 1977, an extensive UNIFAC parameter table was published by *Fredenslund et al. (1977)*. This parameter table has been revised and extended in a series of articles. Recently, the fifth version has been completed *(Hansen et al., 1991)*. In this new version, a total of 223 pairs of group-interaction parameters have been revised or added to the parameter table. Six new main group have been added, such that UNIFAC has been extended to cover mixtures with chlorofluorohydrocarbons, amides, glycol ethers, sulfides, morpholine, and thiophenes.

2.2.2 Estimation of properties important in environment

Relationships

Activity coefficients represent the non-ideal behavior of a solution. By virtue of the activity coefficient, the UNIFAC model can be applied to describe many environmentally important properties, among those are 1-octanol/water partition coefficient, water solubility, and the Henry's law constant. This relationship is clearly shown in Figure 1.

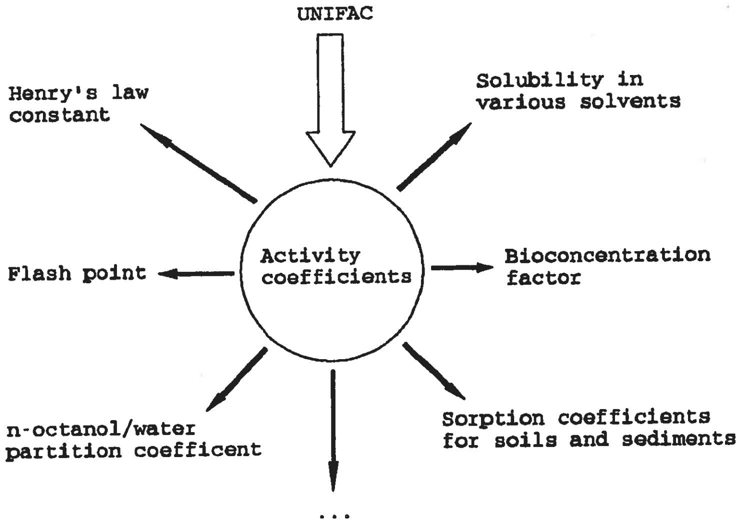

Figure 1. Relating Activity Coefficients with Environmental Properties

Advantage

Since the UNIFAC model has a sound physical background, and the UNIFAC group-interaction parameters are determined from thermodynamically consistency data, the above procedure delivers a more reliable and consistent way to estimate many environmental important properties compared to some other QSAR models.

1-Octanol/water partition coefficient

A detailed discussion of the relationship between activity coefficients and 1-octanol/water partition coefficients has been given by *Lyman et al. (1982)*. According to their work, the following equation is adopted in the calculation of 1-octanol/water partition coefficient:

$$K_{ow} = 0.151\frac{\gamma_i^{w,\infty}}{\gamma_i^{o,\infty}} \qquad (2)$$

Where $\gamma_i^{w,\infty}$ and $\gamma_i^{o,\infty}$ are the infinite dilution activity coefficients of component i in the water phase and the 1-octanol phase, respectively.

Water solubility

The solubility of a chemical in water may be defined as the maximum amount of the chemical that will dissolve in pure water at a specified temperature. According to its definition and considering the density of water at 25⁰C as $5.523\text{x}10^4$ (mol/m^3), we can have

$$C_i^w[mol/m^3, 25°C] = 5.523\times10^4\frac{x_i^w}{1-x_i^w} \qquad (3)$$

where x_i^w is the mole fraction of chemical i in water.

If the water solubility of chemical i is very small, x_i^w can be approximately determined by (which will be discussed in detail in Part II)

$$x_i^w \approx \frac{1}{\gamma_i^{w,\infty}} \qquad (4)$$

Where $\gamma_i^{w,\infty}$ is the infinite dilution activity coefficient of chemical i in water phase and may be calculated from the UNIFAC model.

Otherwise

$$x_i^w = x_i^{oc} \times \frac{\gamma_i^{oc}}{\gamma_i^w} \qquad (5)$$

In this equation, γ_i^{oc} and x_i^{oc} refer the activity coefficient and the mole fraction of chemical i in organic phase, respectively. The UNIFAC model may be used to solve the equation from the binary liquid-liquid equilibrium or solid-liquid equilibrium point of view.

It should be pointed out, that most of the calculations in this work were carried out by use of equations (3) and (4).

In this work, the UNIFAC model, with the latest parameter table *(Hansen et al., 1991)*, has been adopted to determine the activity coefficients of chemicals. Furthermore, through equations (2)-(5), 1-octanol/water partition coefficient and water solubility for the corresponding chemicals are calculated.

Application for logKow

A comparison of the experimental and predicted logKow values for 236 datapoints is given in Appendix A. Figure 2 correspondingly shows the results in a more straightforward way. It can be seen that the experimental and predicted logKow data are in good agreement. However, the deviations increase fast when the logkow values are greater than 6. That indicates that both the accuracy of the UNIFAC model for highly hydrophobic compounds and the quality of the experimental logKow-values in the region above 6 should be looked into more carefully.

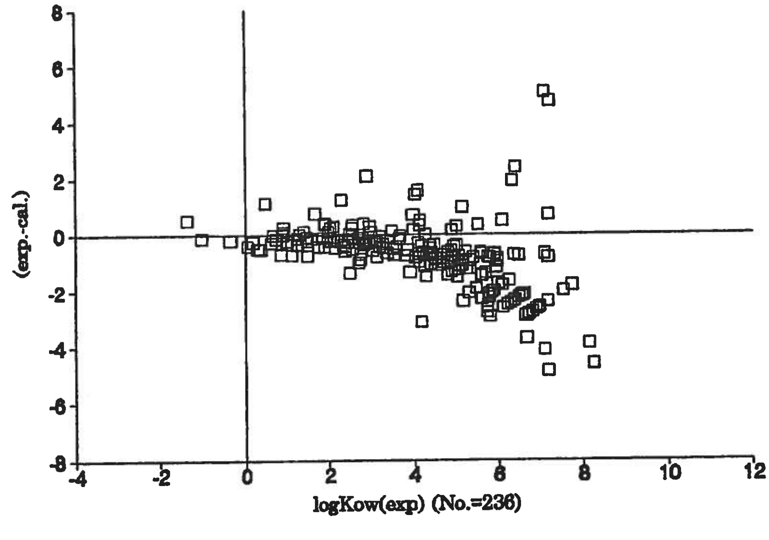

Figure 2. Performance of the Original UNIFAC for LogKow

Performance for water solubility

Figure 3 presents the performance of the UNIFAC model for water solubility. For a set of total 271 datapoints, the results seem satisfactory. Interesting enough, the calculated values depart from the experimental ones when the water solubilities of the chemicals become quite low, which coincides with the situation for high logKow-value.

It may be concluded that 1-octanol/water partition coefficients and aqueous solubilities can be quite good estimated if activity coefficients are available, and activity coefficients for nonelectrolytes can be estimated from chemical structures by means of the UNIFAC model. Hence, this method offers the potential for reasonable estimations of Kow and Cs in the absence of laboratory data.

Drawback

Nevertheless, the UNIFAC group-interaction parameters were determined from vapor-liquid equilibria of binary systems in the whole concentration range, which might restrict the prediction ability of the model at infinite dilution condition, since fluid phase behaviors at infinite dilution are often very different from those at finite concentrations. This drawback will become even more serious when highly hydrophobic systems are dealt with, as already mentioned before. Another limitation of the method is that several functional groups which are of environmental importance are not included in the present UNIFAC parameter table. Obviously, further development might be considered.

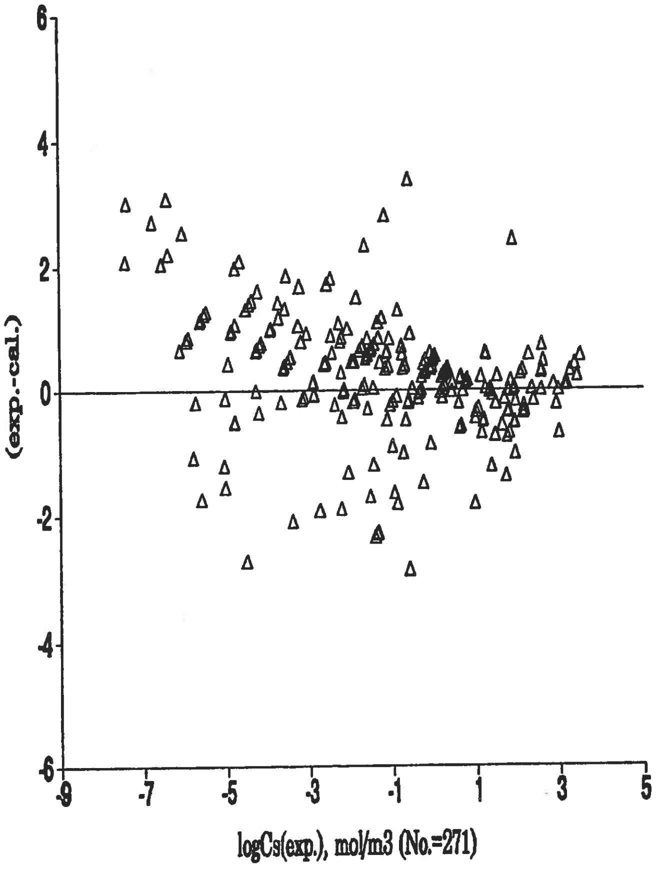

Figure 3. Performance of the Original UNIFAC for Water Solubility

2.3 New development of the UNIFAC model

2.3.1 Experimental information

Infinite dilution activity coefficient

According to its definition, an activity coefficient, γ, is a correction factor compensating for non-ideal behavior. If we use the convention that $\gamma=1$ for the pure components 1 and 2, as the concentration of one component becomes increasingly dilute, the value of γ for this component asymptotically approaches a limiting value, γ^∞, the infinite dilution activity coefficient. Infinite dilution activity coefficients can be obtained in several different ways. The following three approaches have been applied in this work.

(1) Direct experimental measurement

Direct measurement

Static and gas chromatographic methods are commonly used for measuring infinite dilution activity coefficient. Since the accuracy of the static method at the diluted concentration range is not certain, and the method is relatively complicated, much research has been devoted to develop the gas chromatographic method in the last two decades *(Conder and Purnell, 1968; Valentin and Guiochon, 1976; Ruff et al., 1986)*, since this method shows to be a good alternative to the static method. Some infinite dilution activity coefficients can be found in the Dortmund Data Bank *(Gmehling and Onken, 1977)*.

(2) Determination from binary vapor-liquid equilibrium data

From vapor-liquid equilibria

When vapor-liquid equilibrium data are available for a binary system, the activity coefficients at varying concentrations, γ_i, can be directly calculated as follows

$$\gamma_1 = \frac{Py_1}{P_1^0 x_1} \tag{6}$$

and

$$\gamma_2 = \frac{Py_2}{P_2^0 x_2} \tag{7}$$

Where x_i is the mole fraction of component i in liquid phase, y_i is the mole fraction of component i in vapor phase, P_i^0 refers to the vapor pressure of pure liquid i and P is the pressure.

These obtained activity coefficients cover the whole concentration ranges. They may be combined with one of the activity coefficient models, such as Margules, Van Laar, Wilson, NRTL, and UNIQUAC, to compute the infinite dilution activity coefficients of these two components. Also, one can extrapolate them directly to zero concentrations to get infinite dilution activity coefficients. In this work, the infinite dilution activity coefficients are derived by combining the activity coefficients in the whole concentration range with the UNIQUAC model *(Abrams and Prausnitz, 1975).*

One major advantage of this approach is that it is possible to check the reliability of vapor-liquid equilibrium data through a thermodynamic consistency test.

(3) Determination from binary liquid-liquid equilibrium data

From binary liquid-liquid equilibria

For the systems consisting of highly hydrophobic compounds, vapor-liquid equilibrium data are rarely available due to liquid immiscibility. The infinite dilution activity coefficients for these compounds will be estimated from liquid-liquid equilibrium data.

From classical thermodynamics the condition for phase equilibrium of a binary solutions is

$$x_1^I \gamma_1^I = x_1^{II} \gamma_1^{II} \qquad (8)$$

$$x_2^I \gamma_2^I = x_2^{II} \gamma_2^{II}$$

where the superscript I refers to organic phase, the superscript II refers to water phase, and the subscripts 1 and 2 correspond to organic component and water, respectively.

Approximation

For very small mutual solubilities, the following approximations are valid

$$x_1^{II} \approx 0 \Rightarrow x_2^{II} \approx 1 \Rightarrow \gamma_2^{II} \approx 1 \qquad (9)$$

So that,
Similarly, we have

$$x_1^{II}\gamma_1^{II} \approx 1 \Rightarrow \gamma_1^{\infty} \approx \frac{1}{x_1^{II}} \tag{10}$$

$$\gamma_2^{\infty} \approx \frac{1}{x_2^{I}} \tag{11}$$

When mutual solubilities are not small enough to make the above approximations, the UNIQUAC model may be used to solve the activity coefficients from the binary liquid-liquid equilibrium data, if parameters A_{12} and A_{21} of the UNIQUAC model can be found from literatures at the corresponding temperature.

2.3.2 Parameter estimation

242 sets of infinite dilution activity coefficients were obtained and used to estimate new group-interaction parameters especially for aqueous solutions. The group volume and group surface parameters are taken from the original UNIFAC *(Fredenslund et al., 1977)*.

Objective function

The group-interaction parameters presented in this work were estimated by minimization of

$$F_{mm}=\sum [(y_1(cal.)-y_1(\exp.))/\sigma_y]^2+[(P(cal.)-P(\exp.))/\sigma_P]^2 \tag{12}$$

where y_1 is the vapor-phase mole fraction of component 1, P is the pressure, and σ_y and σ_P are weight factors. The Levenberg-Marquardt algorithm was used for the minimization.

New parameters

On the basis of infinite dilution activity coefficients, the group-interaction parameters for 31 pairs of groups have been estimated. Table M-3 in Appendix C gives a list of these groups. Table M-4 in Appendix C lists their group-interaction parameters. It should be noted that the group-interaction parameters for Br, C≡C, and HCOO with H_2O are here included for the first time.

2.3.3 Results

Improvement for logKow

Using the new group-interaction parameters, logKow values for some organic compounds have been calculated and presented in Appendix B. The results from the original group-interaction parameters are also shown for comparison. It shows that the deviations between calculated and experimental values have been dramatically reduced by using the group-interaction parameters based on infinite dilution information, and also, that the UNIFAC model now can very well represent the properties for systems containing Br and C≡C groups.

Improvement for water solubility

Results for water solubilities are clearly shown in Figure 4, where the squares indicate the calculated results from the original UNIFAC group-interaction parameters. The crosses represent the computed results from our new group-interaction parameters. It can be seen that our new group-interaction parameters are to be much preferred for all the points.

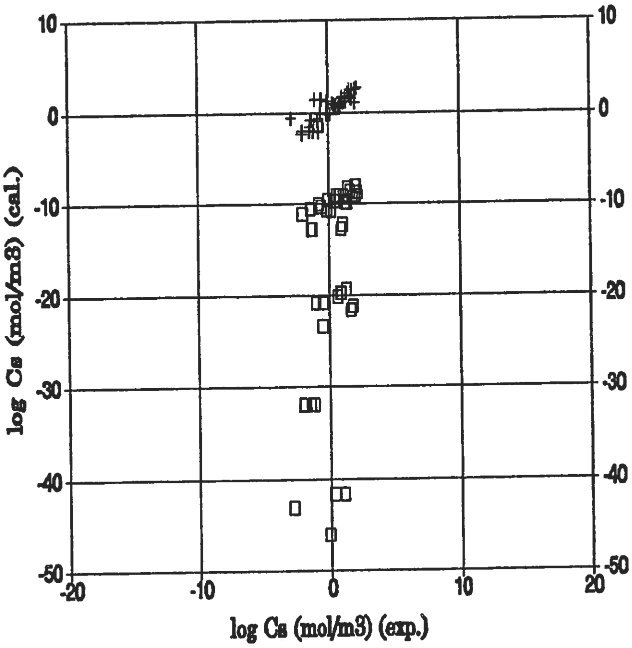

Figure 4. Comparison of the Original and the Improved UNIFAC for Water Solubilities

2.4 Summary

New developments

It has been shown that the UNIFAC approach is a useful technique for prediction of 1-octanol/water partition coefficients and aqueous solubilities. The original UNIFAC group-interaction parameters are obtained from binary vapor-liquid equilibria in the whole concentration range, therefore, in some case, the model performs not so well at the infinite dilution concentration region, which is an even more serious problem for systems containing highly hydrophobic compounds. Therefore, a new set of group-interaction parameters has been developed. The new parameters are estimated from the infinite dilution activity coefficients of compounds in aqueous solution. It has been demonstrated that this new set of group-interaction parameters has greatly improved the predictive accuracy of the UNIFAC model for aqueous solutions, and extended the model to the systems containing Br, $C{\equiv}C$, and HCOO groups.

Future work

Obviously, since the UNIFAC model is originally developed for chemical engineering purposes, some modifications are necessary in order to apply the model for prediction of environmental exposure assessment related parameters. The UNIFAC model approximately treats functional groups the same, no matter what functional group is adjacent. Thus, the model can not be used when two strong groups are adjacent to each other ("proximity effects"). Also, the model can not distinguish between isomers. Furthermore, the group-interaction parameters are not available for some environmentally important compounds. Nevertheless, the UNIFAC model is founded on a sound thermodynamic basis and does offer the potential for reasonable predictions of Kow and Cs in the absence of laboratory data. Some promising perspectives of further development for the UNIFAC model can already be seen from the second part of this work. More work is in progress at our institute in order to further improve the applicability of the UNIFAC model for environmental applications.

3 Environmental exposure assessment

3.1 General principles

Objective

The objective of the exposure assessment is to identify a potential release of a substance into the environment and to predict environmental concentrations, PEC, as a function of time and location.

The general procedure consists of the following steps:

Procedures

1. Identification of potential and/or possibility for environmental release

2. Identification of receiving environmental compartment(s)

3. Estimation of rates of release into the environmental compartment(s) of concern

4. Estimation of the distribution and environmental concentrations as a function of time and location

Life cycle should be considered

For the exposure assessment involving the stages shown above the whole life cycle of a substance should be considered with respect to the potential for environmental exposure. The life cycle of a chemical includes the following stages:

production
processing or formulation
industrial use
private or consumer use
recycling
disposal and waste treatment

The exposure routes of a substance are schematically given in Figure 5.

According to the context of the seventh amendment of directive 67/548/EEC, the exposure considerations should be restricted to the designated use of a substances; accidents are not taken into account. However, indirect release, such as might arise from land-spreading sewage sludge, are considered.

3.2 Data needs for environmental exposure assessment

Required information

Generally speaking, there are two types of data needs for exposure assessment:

A) Release estimates need information on:

production process
subsequent life cycle of the substance

B) Prediction of environmental concentration needs information on:

emission rate and emission concentration
physico-chemical properties related to the environmental fate
degradation data
environmental data (e.g. size of compartments, temperature).

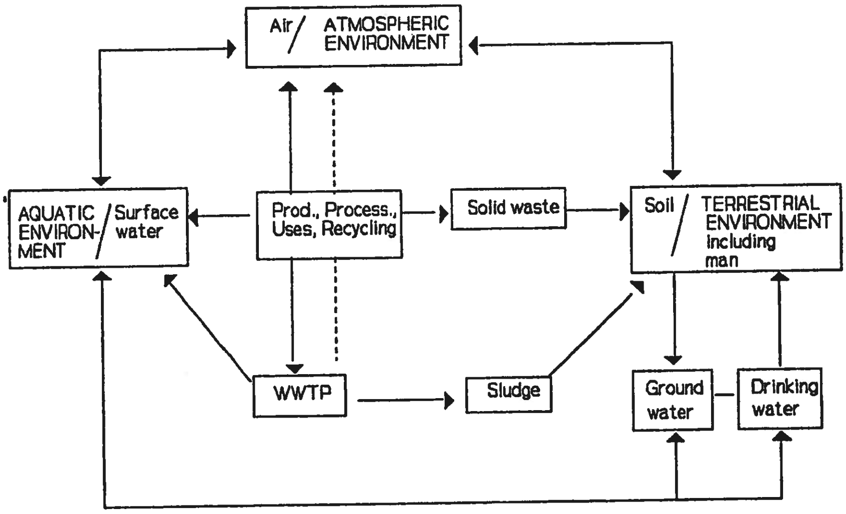

Figure 5. Exposure routes

3.3 Models for environmental exposure analysis

Generally speaking

The key step in exposure assessment is the use of a transport and transformation model to quantify the movement of contaminants from the source, through the environment, to the target populations. Processes such as accumulation, soil sorption, abiotic (hydrolysis, photolysis) and biotic (microbial) transformation, propagation, and distribution will contribute to the effective exposure level. Several models of varying complexity have been developed to calculate and predict the distribution of chemicals in the environment. Most of them are derived from the Mackay model *(Mackay 1979, Mackay and Paterson 1981, 1982)* to describe the environmental compartment (air, soil, water, biota) in which the chemical are most likely to be found. Based on the concept of fugacity, models were described for four levels of increasing complexity. Level I assumes equilibrium between all compartment, level II includes transformation and steady-state input of the contaminant, level III is extended to slow transport processes between the compartments, and level IV allows variation of fugacity, input rate, and concentration with time.

In december 1991 an OECD workshop on exposure models with respect to "SIDS (Screening Information Data Sets) chemicals" was held, aiming at identifying appropriate simple methods for release estimates, fate models and indirect exposure, i.e. exposure to man via food and water (OECD Secretariat, 1992).

Three local models and one global model

A set of four exposure models was decided upon with respect to "SIDS chemicals" - three local models, each concerned with a single environmental phase, and one global model. The three local models are: a water model, an air model, and a soil model. Local models are those which are concerned with the environment close to the release site, and with a short time scale after the release. It was recommended that a Mackay level III model *(Mackay,D. et al., 1992)* should be used as the basis of the global model. Global models are those which are concerned with the longer term, steady state behaviour of a chemical, and are multi-media.

4 Computer models for environmental exposure assessment

The real environment is very complex, and only small sections of it, such as a pond or a stretch of river, can be modeled adequately. Complex models are, within the context of the chemicals regulation, unlikely to play a significant role.

Concept of evaluative model

In order to predict the environmental distribution and fate of chemical substances, *Baughman and Lassiter (1978)* introduced the concept of an evaluative model with the aim of developing a quantitative approach for exposure estimation. With the understanding that in the evaluative model no attempt is made to simulate the real environment, but to predict partition possibilities into each environmental compartment. Successively *Mackay and Paterson (1981)* proposed the "fugacity model" to calculate the relative amount of substance that will partition into each environmental compartment.

4.1 Fugacity model

Two sets of controlling factors

Chemical fate is apparently controlled by two sets of factors, the inherent properties of the chemical (especially solubility in water, vapor pressure, reactivity, etc.) and the nature or properties of the environment into which the chemical is discharged (e.g. temperature, flows of air, water and solids and the composition of these phases). Whereas these latter factors vary from location to location, the chemical properties are universal. There is thus incentive to separate these factors and conduct chemical fate assessments in a common "evaluative" environment as a prelude to region-specific environments. Assessments performed in this way can be shared internationally.

Generic scenario

In fugacity model *(Mackay et al. 1992)*, the evaluative or generic environment treated is an area of 100,000 km^2 which is about the area of Greece, twice of the area of Denmark. Most regions of political interest are small multiples of this area, for example Italy is three such areas.

Air, water and soil

The atmospheric height is selected as a fairly arbitrary 1000 m reflecting that region of the troposphere which is most affected by local air emissions. A water surface area of 10% or 10,000 km^2 is used, with a water depth of 20 m. The water volume is thus $2x10^{11}$ m^3. The soil is viewed as being well-mixed to a depth of 10 cm and is considered to be 2% organic carbon. It has a volume of $9x10^9$ m^3. The bottom sediment has the same area as the water, a depth of 1 cm and an organic carbon content of 4%. It thus has a volume of 10^8 m^3.

Suspended matter and fish

Suspended matter in water is often an important medium when compared in sorbing capacity to that of water. It is treated as having 20% organic carbon and being present at a volume fraction in the water of $5x10^{-6}$, i.e. approximately 5 mg/L. Fish are also included at an entirely arbitrary volume fraction of 10^{-6} and are assumed to contain 5% lipid which is equivalent in solvent properties to octanol. These two phases are small in volume and rarely contain an appreciable fraction of the chemical present, but it is in these phases that the highest concentrations of chemical often exist.

Aerosol particles

A seventh phase which is introduced later, is aerosol particles with a volume fraction in air of $2x10^{-11}$, i.e. approximately 30 µg/m3.

These dimensions and properties are summarized in Table 1. The user may modify these dimensions to reflect conditions in any specific area of interest.

Fugacity represents escaping tendency

Fugacity can be regarded as the "escaping tendency" of a chemical substance from a phase, it is expressed in units of pressure and is linearly proportional to concentration. From classical thermodynamics, if a chemical is at equilibrium between all phases, then the fugacities of the chemical are equal in all phases.

One can consider each environmental compartment as a phase and there are no limitations about the number of compartments to be introduced into the model or about the volume of each compartment.

Table 1. Compartment dimensions and properties for Level I and II calculations

Compartment	Air	Water	Soil	Sediment	Susp. Sed.	Fish
Volume (m3)	10^{14}	$2x10^{11}$	$9x10^{9}$	10^{8}	10^{6}	$2x10^{5}$
Depth (m)	1000	20	0.1	0.01	-	-
Area (m2)	$100x10^{9}$	$10x10^{9}$	$90x10^{9}$	$10x10^{9}$	-	-
Fraction OC	-	-	0.02	0.04	0.2	-
Density (kg/m3)	1.2	1000	2400	2400	1500	1000
Advection residence time (hours)	100	1000	-	50,000	-	-
Advective flow (m3/h)	10^{12}	$2x10^{8}$	-	2000	-	-

Equilibrium criterion

At equilibrium:

$$f_1 = f_2 = \dots\dots\dots = f_i \qquad (13)$$

where f_i is the fugacity of a substance from the compartment "i", moreover:

$$f_i = \frac{C_i}{Z_i} \qquad (14)$$

where C_i is the concentration in the compartment "i" and Z_i is the fugacity capacity constant.

Therefore, if one wants to calculate how a substance will partition, one has to find Z for the substance and for each environmental compartment.

If there are two compartments "i" and "j" at equilibrium:

$$f_i = f_j = \frac{C_i}{Z_i} = \frac{C_j}{Z_j} \qquad (15)$$

thus

$$\frac{Z_i}{Z_j} = \frac{C_i}{C_j} = K_{ij} \tag{16}$$

where K_{ij} is the partition coefficient controlling the distribution between the two compartments.

From the Eq.(16):

$$Z_i = K_{ij} \cdot Z_j \tag{17}$$

Capacity of compartment

Therefore one can easily introduce a new compartment "i" in the fugacity model by calculating Z_i form the Eq.(17) if one knows the partition coefficient between this new phase and a compartment "j" and the capacity of this last compartment (Z_j). The capacities of the main environmental compartments are, according to *Mackay and Peterson (1981),* the following:

Air	$Za = 1/RT$
Water	$Z_W = 1/H$
Soil	$Zs = K_p \rho_s/H$
Biota	$Z_B = K_B \rho_B/H$
Pure solute	$Z_P = 1/P^s v_s$

where R is the universal gas constant (8.314 $Pa \bullet m^3 \bullet mol^{-1} \bullet K^{-1}$), T is the temperature (K), H is Henry's law constant ($Pa \bullet m^3 \bullet mol^{-1}$), K_p is the soil sorption coefficient, H is Henry's law constant, K_B is the biosorption coefficient, ρ_B is the biota density, P^s is the vapor pressure, and v_s is the solute molar volume.

It should be noted that in Eq.(17) partition coefficients are expressed as the ratio between weigh•volume^{-1} concentrations (i.e. $mg \bullet l^{-1}$; $mg \bullet m^{-3}$). If the concentrations are expressed as weight• weight^{-1} the density of the phase (ρ_i) must be introduced. Figure 6 demonstrates various relationships between fugacity capacities (Z) and physical properties.

The fugacity model is described of four levels for increasing complexity *(Mackay,D., 1979; Mackay and Paterson, 1981, 1982; Mackay et al., 1992).*

Level I

Equilibrium partitioning

The Level I calculation describes the equilibrium partitioning of a given amount (an arbitrary 100,000 kg or 100 tonnes) of chemical between the six media as listed in Table 1.

The Level I calculation proceeds by deducing thermodynamic partitioning expressions of fugacity capacities (Z) for each medium. The assumed temperature is 25°C. The fugacity in units of Pa common to all media is deduced as

$$f = M/\Sigma V_i Z_i \tag{18}$$

where M is the total amount of chemical (mol), V_i is the medium volume (m^3) and Z_i is the corresponding fugacity capacity (mol/-m^3Pa) for the chemical in that medium.

Characteristics of substances are needed

The data needed for Level I calculation are molecular mass, water solubility, vapor pressure, and octanol-water partition coefficient at 25°C. The information obtained from this calculation includes the concentrations, amounts and distribution between the six media. This information is useful as an indication of the relative concentrations, and of the likely media of accumulation.

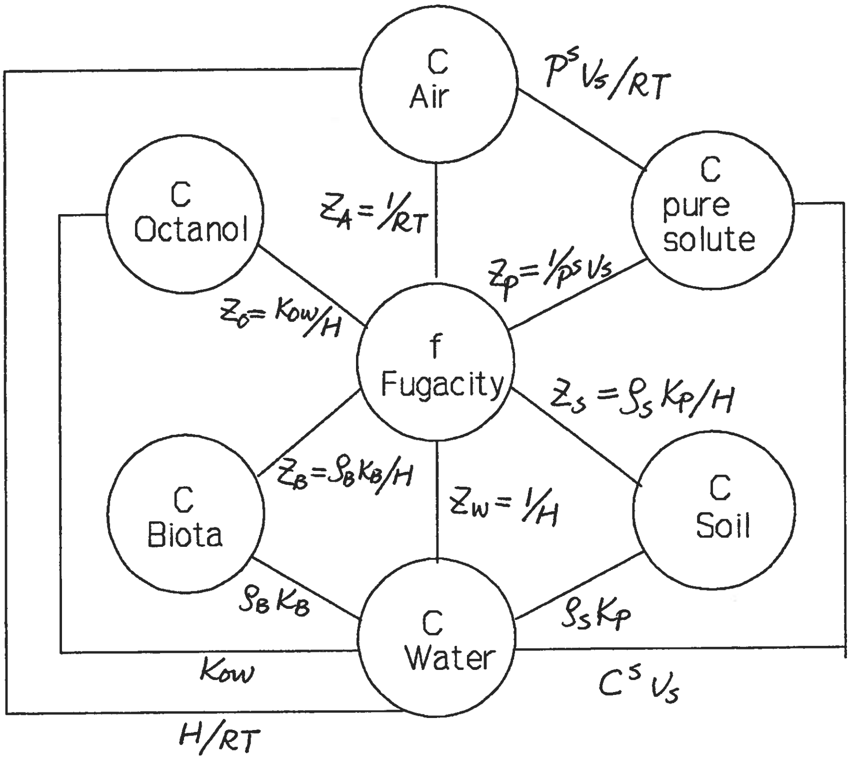

Figure 6. Relationships between fugacity capacity (Z) and physical properties. Symbols are defined in the text. Modified from *Calamari et al. (1987).*

Level II

Steady-state and equilibrium condition

The Level II calculation simulates a situation in which chemical is continuously discharged into the multimedia environment and achieves a steady-state and equilibrium condition at which input and output rates are equal. The task is to deduce the rates of loss by reaction and advection.

Degradation is considered

From degradation reaction rate data for each chemical a first order rate constant or half-life is selected for each medium. The rate constants k h^{-1} are used to calculate reaction D values for each medium D_R as $V_iZ_ik_i$. The D value for loss by advection D_A is equal to the advection rate Gi multiplied by fugacity capacity Z_i. At steady-state, equilibrium conditions the input E mol/h can be equated to the sum of the output rates, from which the common fugacity can be calculated as

$$f = E \,/\, (\Sigma D_A + \Sigma D_R) \tag{19}$$

For Level I and II calculations, only partitioning into solid phases in soil and sediments are considered, i.e. "pore air or water" are ignored.

Level III

Steady-state system with nonequilibrium distribution

The Level III model introduces interphase transfer resistance and describes a steady-state system with nonequilibrium distribution in which each phase may have a different fugacity. Emissions may be into one or more phases. In the interests of algebraic simplicity only four primary media are treated in Level III, air, water, sediment, and soil.

"Bulk phase" is introduced

"Bulk phase" Z values are introduced for the four media *(Mackay and Paterson, 1991)*. Since include the contribution of dispersed phases within each medium, these "bulk phase" values are slightly different from the Level I and Level II "pure phase" values. 12 intermedia transport velocity parameters designated U_1 to U_{12} are applied to all chemicals for describing the various diffusive and non-diffusive processes. These parameters are used to calculate seven intermedia transport D values. The total phase volumes in the Level III are presented in Table 2. It can be seen that they are different from those in the Level I and Level II.

Intermedia transport data are additionally needed

The new information from the Level III calculation is the intermedia transport data, i.e. the extent to which chemical discharged into one medium tends to migrate into another. Thus, the fate of a chemical is controlled by:

its intermedia partitioning characteristics (Z values)
its reaction and advection D values
its intermedia transport D values
and how it enters the environment.

Table 2. Bulk compartment dimensions and volume fractions v for Level III calculations

Air		Total volume 10^{14} m^3
	Air phase	10^{14} m^3
	Aerosol phase	2000 m^3 (v=2x10^{-11})
Water		Total volume 2x10^{11} m^3
	Water phase	2x10^{11} m^3
	Suspended sediment phase	10x10^6 m^3 (v=5x10^{-6})
	Fish phase	2x10^5 m^3 (v=1x10^{-6})
Soil		Total volume 18x10^9 m^3
	Air phase	3.6x10^9 m^3 (v=0.2)
	Water phase	5.4x10^9 m^3 (v=0.3)
	Solid phase	9.0x10^9 m^3 (v=0.5)
Sediment		Total volume 500x10^6 m^3
	Water phase	400x10^6 m^3 (v=0.8)
	Solid phase	100x10^6 m^3 (v=0.2)

Level IV

Unsteady-state nonequilibrium conditions

Level IV introduces the concept of emissions that change with time, causing nonequilibrium, unsteady state conditions. If emissions are constant, it will approach the Level III steady-state condition at long times. The objective of Level IV is to provide a simple but physically realistic method for calculating the interphase resistances.

The interest raised by the fugacity approach was high and a number of papers were published on this subject *(e.g., Neely and Blau, 1985, Calamari et al., 1987, and Wood et al., 1982)*. The fugacity Level III model *(Mackay et al., 1992)* is even more adopted as the basis of the global model for exposure assessment at the OECD Workshop held in December, 1991 in Berlin. The several computer programs, which we are going to discuss in the following, are also more or less based on the fugacity approach.

4.2 The Dutch program: *DRANC*

DRANC is developed for the local scale in the Netherlands

DRANC is a computer program for the Dutch Risk Assessment of New Chemical substances. The program is developed for the assessment of hazards and risks of new chemical substances (level 0, 1-100 ton/year) in the Netherlands. This system includes assessment of emissions, environmental concentrations and effects. Emissions are regarded as point sources, and exposure assessment is carried out on a local scale.

The distribution routes of *DRANC* is:

Emission -> Distribution -> Concentration -> Exposure

Emissions

The expert system PECker *(Van der Poel, 1991)* estimates emissions of new substances according to the results of extensive industry category studies concerning losses during production, processing, use, waste processing and recycling of defined groups of substances. Seven groups of organic chemicals are distinguished in the estimation system:

use category

- textile dyes;
- paper chemicals;
- photochemicals;
- additives for metal working/hydraulic fluids;
- intermediate products;
- plastic additives;
- general, for all other chemicals.

Distribution

The main assumptions made in the assessment system with regard to distribution of substances in the environment are:

- Steady-state concentrations in the environment are regarded, although it may take many years before these concentrations will be reached;
- Target organisms are: micro-organisms in a waste water treatment plant, aquatic organisms in surface water, and human beings.

In order to estimate the exposure of the target organisms, the main routes of chemicals in the environment to these organisms are determined and modelled according to some concepts which are summarized below:

Exposure routes

- Emissions are considered to originate from point sources, which produce a continuous load toward water. If emissions vary through time, the highest occurring emission is chosen;
- All water emissions are assumed to be collected and passed through a waste water treatment plant (WWTP). Depending on the characteristics of the chemical, removal may occur by biodegradation, adsorption to sludge or volatilization. The effluent is diluted with surface water. Sludge from the WWTP is used as fertilizer on agricultural land and grassland;
- Only surface water is used in the preparation of drinking water. In the present state, only the particulate fraction of chemicals is removed during preparation;
- Concentrations in human food are estimated by means of bioconcentration factors from surface water to fish, and from soil to agricultural crops, meat and dairy products. Bioconcentration factors are estimated on the basis of the octanol/water partition coefficient of a substance;
- The total daily intake by human beings is the sum of the intake of different food media: drinking water, fish, crops, meat and dairy products.

Effects and hazard assessment

Extrapolation method is used

For the aquatic organisms, the modified extrapolation method of the EPA is used *(Vermeire et al., 1992; Slooff, 1992)*. Depending on the availability of LC50 values and NOEC's, an extrapolation factor of 10, 100 or 1000 is applied to the lowest LC50 or NOEC. The resulting no-effect concentration is then compared to the predicted environmental concentration, leading to a Hazard Quotient for aquatic organisms.

The no-effect concentration for micro-organisms in a WWTP is extrapolated from IC50 values. An extrapolation factor of 10 is applied, as estimated by *Roghair (1988)*. The resulting no-effect concentration is then compared to the concentration in the influent of the WWTP.

For man, the dose without adverse effect (DWE) as established in an experimental animal study, usually a 28-day test with rats, is directly compared to the predicted total daily intake, without further extrapolation. The resulting 'Margin of Safety' indicates the degree of hazard.

Input information

The input data for *DRANC* are physical and chemical properties of the chemical, toxicological data of the chemical, emission data, WWTP and dilution data, model parameters of the WWTP. Default values are given for all these data in *DRANC*.

4.3 The Canadian program: *STP*

STP model is based on the fugacity model concept

The program *STP* performs a steady-state model which seeks to correlate or predict the fate of organic chemicals in a biological waste water treatment plant, or a sewage treatment plant (STP). The model is based on the fugacity modelling concept *(Mackay, D. and Paterson, S., 1981)*. The input parameters are the physical properties of the chemical (molecular weight, vapor pressure, solubility in water, octanol/water partition coefficient, and biodegradation rate constant) and the relevant design and operating parameters of the biological waste water treatment plant (water flow rates, solids content in process streams and in reactors, volatile matter content of solids, and geometry of the vessels). The model estimates the relative amounts of chemical which are stripped or volatilized, sorbed to sludge, biodegraded, and discharged in the effluent water. The program gives as output a prediction of the chemical fluxes in all process streams, the chemical concentrations in the water, air, and sludge phases, and a statement of mass balance.

Biodegradation rate constant is a sensitive variable in STP

Validation of the model has been attempted by comparing the model output with data from a laboratory scale treatment system, with output from other similar models, and with data from full scale plant. The most critical variable is the biodegradation rate constant and its dependence on biomass concentration.

Model applicability

However, as authors have pointed out *(Clark, B. et al., 1989)*, it is unlikely that any simple mathematical model will ever accurately predict the fate of organic chemicals in STPs. Flows and concentrations vary continuously as do temperatures and the nature of the microbial community which is primarily responsible for sorption and degradation. The best that can be hoped for is that the model gives a reasonable representation of long term or average fate, and enables the dominant processes and fate mechanisms to be identified.

4.4 The Danish program: *Fugacity I*

The program *Fugacity I* is a dBase IV translation of the program written by *Mackay and Paterson (1990)*. The program uses arrays, and for this reason dBase IV is required *(Niemelä, J., 1991)*. The needed input parameters are:

Not much information is needed in Fugacity I

Temperature
Molecular weight
Vapor pressure
Water solubility
Log octanol/water partition coefficient
Amount of chemical.

After fugacity calculations are performed, the partitioning of the chemical into four compartments, Air, Water, Soil, and Sediment is shown in percent.

4.5 The German program: *SAMS*

SAMS includes only local models

SAMS is the short form of the Screening Assessment Model System. The system includes three local models, each concerned for air, water, or soil. As it has been clarified in the last chapter, local models are those which are concerned with the environment close to the release site.

Release sources

Chemicals are released into the atmosphere from various differing types of sources: solvents from vents, diffuse emissions from traffic, manufacturing or households, or by spraying of pesticides. The release heights varies from ground level to effective stack heights. Chemicals are distributed by atmospheric dispersion and transport and removed by photodegradation and deposition. The AIR model calculates the steady-state concentration after areal or point source releases using long-term, average weather statistics *(Trenkle and Münzer, 1987)*. The approach for calculation of concentration is dependent on the type of release.

The RIVER model was developed to evaluate chemicals fate in surface water bodies after continuous releases either from waste water treatment plants or directly. Downstream concentrations are calculated assuming steady-state conditions for water and chemical flow.

Advection, dispersion, volatilisation, and degradation are included

Various processes determine the transport and fate of the chemical. Advection, dispersion, volatilisation and degradation are included in the RIVER model. Sediment is not included as a compartment in the RIVER model. The transport after short-term releases, e.g. after an incidental input, can not be predicted due to the steady-state assumptions. The output of the RIVER model are:

- Concentration in the fluid phase (water+suspended matter)
- Concentration of the sorbed chemical
- Total input
- Total initial concentration C_0
- Dilution factor D_f
- Inventory within the river
- Bioconcentration in fish at the release point
- Bioconcentration in fish at the outflow of the river
- Volatisation rate k_V and sorption coefficient K_D
- Total losses along the river.

SOIL is a one-dimensional vertical dynamic model

The model SOIL describes the transport of chemicals in the unsaturated soil zone in order to predict the behavior of chemicals under various environmental scenarios (soil type, climate and chemical input). SOIL is a one-dimensional vertical dynamic model connecting substance data with soil and climate parameters. The model assumes a time constant vertical water flow in a one-dimensional soil column and an instantaneous equilibrium partitioning of the chemical between adsorbed, dissolved and gaseous phase *(Matties et al. 1987, Behrendt et al. 1990).* Concentration profiles are calculated and leaching of chemicals, volatilisation and accumulation in soil are estimated. The concentrations in the top layer are calculated for comparison with the hazard values for microorganisms and that in the bottom layer for estimating the contamination of groundwater.

The input data for *SAMS* are molecular weight, solubility in water, vapor pressure, melting point, boiling point, Log (octanol/-water partition coefficient), and biodegradation rate constant of the chemical.

4.6 The American program: *PDM3*

Screening level exposure assessment model

PDM3 is a PC based program for performing screening level exposure assessments. The program *PDM3* predicts how many days per year a chemical concentration of concern level in an ambient water body will be exceeded after being discharged from an industrial facility. The result is dependent on the following factors:

- Amount of chemical discharged;
- Effluent flow rate;
- Receiving stream flow rates;
- Variability of stream flow rates;
- Concentration of concern level.

Site-specific case

There are two options to *PDM3*. Option 1 addresses site-specific cases. It performs analysis of a specific reach to the real streams in USA. Therefore, this option is not suitable for the situation in other countries.

SIC information is known

Option 2 deals with cases where the location of the chemical loading is unknown and only the SIC grouping of the industrial facility is known. It corresponds to a worse case or average case probability. To use Option 2, the user must first select one of the 41 listed industrial groupings and then input the number of release days, the chemical loading, and the Concentration of Concern, COC (e.g. 0.1, 1.0, 10 µg/l). *PDM3* will estimate the percent of year exceeded and the days/year exceeded for each COC level entered.

5 Model testing
---- the EEC working group exercise

Although there are a number of computerised exposure models available, they are used by various institutions for different purposes, and their applicability is greatly dependent on the availability of the data needed and on the purposes for which the models have been developed.

The EEC working group

Therefore, it has been decided during the EEC working group meeting (which was held in Copenhagen in July, 1992), that programs of *DRANC, STP, SAMS, PDM3,* and Mackay III were selected for being testing with several selected substances. Among them, models for the elimination in sewage treatment plants was seen to be of priority. The result of this exercise will be incorporated in the model recommendations within the EEC guidance document for environmental exposure assessment of new notified chemicals.

5.1 12 Selected chemicals

12 substances were selected to be used for the model exercise. The selection of the substances include both new notified substances and existing substances. The selection of existing substances provides the possibility to compare the model results with some monitoring data later.

Available information

Formulae, the data of molecular weight, melting point, boiling point, vapor pressure, water solubility, log octanol/water partition coefficient, and degradation rate constant, and uses for these 12 substances as available in the notification dossiers are summarized and presented in Appendix D.

Emission information

In order to keep it simple for the comparison, emission rate of 1 kg/day and emission concentration of 10 mg/l should be used for all 12 substances, if these values were necessary for employment of the models.

5.2 Model exercise

Elimination through a WWTP is focused

Modelling the elimination of a chemical in a WWTP is focused in this work. Based on this priority and the comparability of model results, the calculations for the 12 substances have been carried out by using programs *DRANC, STP* and *Fugacity I.* Table 3, 4, 5 presents obtained results from *DRANC, Fugacity I,* and *STP,* respectively. According to the results, the predicted governing

Table 3. Calculation results of *DRANC*

Compound No.	Fate of chemicals in WWTP, %			
	Air	Water effluent	Sludge	Degraded
1	0.1	4.9	87.6	7.5
2	54.8	12	33.2	0.0
3 (low VP)	0.0	5.5	94.5	0.0
3 (high VP)	0.1	5.4	94.4	0.0
4	0.0	4.9	95.1	0.0
5	4.0	99.5	0.1	0.0
6	0.1	8.8	8.7	82.4
7	0.8	99.2	0.0	0.0
8	0.0	94.9	5.1	0.0
9	0.0	9,6	0.0	90.4
10	72.7	5.0	22.4	0.0
11	0.0	78.7	21.4	0.0
12	1.3	96.3	2.4	0.0

Table 4. Calculation results of *Fugacity I*

Compound No.	Percent of chemicals distributed in			
	Air	Water	Soil	Sediment
1	1.87	1.21	50.13	46.79
2	96.73	1.28	1.03	0.96
3 (low VP)	0.31	0.52	51.3	47.88
3 (high VP)	1.05	0.51	50.92	47.52
4	0.04	0.03	51.69	48.24
5	4.41	95.41	0.09	0.09
6	6.99	72.4	10.66	9.95
7	8.46	91.47	0.04	0.04
8	0.37	90.86	4.53	4.23
9	0.01	99.9	0.05	0.04
10	99.63	0.19	0.09	0.09
11	0.0012	67.41	16.86	15.73
12	13.02	83.31	1.9	1.77

Table 5. Calculation results of *STP*

Percent in	1	2	3	4	5	6
Primary sludge	36.69	17.44	58.75	59.84	0.28	4.38
Waste sludge	1.85	7.40	32.81	33.13	1.52	4.09
Primary vola.	5.93e-3	0.84	1.71e-3	1.99e-4	7.15e-3	1.38e-2
Settling vola.	1.18e-3	1.31	3.78e-3	4.38e-4	1.94e-2	3.62e-2
Aeration offgas	3.51e-3	31.98	9.98e-3	1.23e-3	4.82e-2	0.09
Primary biod.	35.95	5.24e-2	0.14	0.14	2.94e-2	0.28
Settling biod.	1.73	1.56e-2	6.07e-2	0.061	1.98e-2	0.20
Aeration biod.	23.23	0.21	0.80	0.80	0.26	2.68
Final water eff.	0.54	40.75	7.41	6.02	97.82	88.23
Total removal	99.46	59.25	92.58	93.98	2.18	11.77
Total biod.	60.91	0.27	1.0	1.01	0.31	3.17

Table 5. Calculation results of *STP* (continued)

Percent in	7	8	9	10	11	12
Primary sludge	0.26	1.72	0.26	12.16	6.95	0.93
Waste sludge	1.51	2.47	1.49	1.55	5.83	1.95
Primary vola.	1.42e-2	6.19e-4	1.40e-5	1.04	2.37e-6	2.36e-2
Settling vola.	3.86e-2	1.68e-3	3.78e-5	0.46	6.32e-6	6.40e-2
Aeration offgas	9.63e-2	4.15e-3	9.31e-5	71.67	1.56e-5	0.16
Primary biod.	1.47e-2	1.79e-2	0.14	4.07e-2	0.11	1.61e-2
Settling biod.	7.62e-3	9.28e-3	9.43e-2	3.49e-3	0.077	8.36e-3
Aeration biod.	0.10	0.12	1.24	4.62e-2	1.01	0.11
Final water eff.	97.96	95.65	96.76	13.03	86.02	96.74
Total removal	2.04	4.35	3.23	86.97	13.98	3.26
Total biod.	0.12	0.15	1.48	0.09	1.20	0.13

Table 6. Governing Compartments in *DRANC, Fugacity I,* and *STP*

Compound No.	DRANC	Fugacity I	STP
1	Sludge	Soil+Sediment	Sludge + degr.
2	Air+Sludge	Air	Air+Water+Sludge
3	Sludge	Soil+Sediment	Sludge
4	Sludge	Soil+Sediment	Sludge
5	Water	Water	Water
6	Degr.	Water	Water
7	Water	Water	Water
8	Water	Water	Water
9	Degr.	Water	Water
10	Air+Sludge	Air	Air+Sludge
11	Sludge+Degr.	Water+Soil	Water+Sludge
12	Water	Water	Water

Governing compartments

compartments (in which the chemicals are mostly distributed) for the 12 substances are listed in Table 6 for comparison.

Interesting enough, if we consider "soil + sediment" compartment in Fugacity I as the same as "sludge" compartment in DRANC and STP, three program give the same governing compartments for compound no. 3, 4, 5, 7, 8, and 12.

For compound no.6, 9, and 11, Fugacity I and STP agree with each other, but not with DRANC. It is shown that degradation plays a great role in DRANC for these three compounds.

For compound no. 10, agreement is achieved by DRANC and STP. But, for compound no.1, DRANC agrees with Fugacity I instead.

And, for compound no. 2, each model seems having its own favorite compartments.

Looking at the above results carefully, one can find that degradation process is the major divergence between these three models.

Analysis of the results

Fugacity I only considers equilibrium partitioning of a chemical in between air, water, soil, and sediment compartments. No degradation process is included. Go a step further, DRANC attempts to predict the fate of a chemical as removed to air or sludge phase, or degraded in WWTP, or remained in water phase. But, the biodegradability of a chemical is very roughly drawn as ready biodegradation or not-ready biodegradation in DRANC. STP aims to give a detailed description for a sewage treatment plant, and biodegradation process is modelled in three stages: primary biodegradation, settling biodegradation, and aeration biodegradation. Half-life time,$t_{½}$, of a chemical, in hours, is applied in STP. Therefore, STP requires more critical restriction for a chemical being ready biodegradation. This explains why compound no.6, 9, and 11 are mainly degraded according to DRANC, but remained in water phase following the STP.

Another interesting point is that Fugacity I overweighs vapor pressure compared to DRANC and STP. Vapor pressure for compound no.2 and 10 are 38 Pa and 248 Pa, respectively, much higher than the other compounds which have similar magnitude of water solubilities. Fugacity I predicts that 96.73% of compound no.2 and 99.63% of compound no.10 will present in air phase, which is significantly higher than those from DRANC and STP.

Compound no.1 has a very high Log octanol/water partition coefficient (log Pow = 5.72), a low vapor pressure (VP = 10^{-4}), and a very low half-life time ($t_{½}$ = 0.57 days). The degree of ready biodegradation for this chemical is higher than those of the others. Thus, The odd result obtained for compound no.1 probably reflects the difference of the sensitivity of these three models to the physical properties of the chemical.

DRANC is a practically employable program, and Fugacity I might be used as a screening model

In summary, although Fugacity I has a very simple model structure, it can give reasonable comparative predictions in many cases, and no any biodegradation data are needed. STP gives a detailed description of a sewage treatment plant and is quite sensitive to biodegradation data of chemicals. Very unfortunately, there are not so many accurate biodegradation data available at present, which will restrict the applicability of STP model. The DRANC model is very user friendly, relatively simple, and only requires qualitative biodegradation data. Therefore, it might be concluded that DRANC is a practically employable exposure assessment program at the present stage, and Fugacity I might be used as a screening model.

5.3 Investigation of the Ispra WWTP removal rate table

It is described in the guidance document that, if no other specific data for emission and environmental conditions are known, the following scenario should be used for calculation of the realistic worst-case initial environmental concentrations, IEC, in mg/l:

Initial environmental concentration

$$IEC = \frac{E \times 10\ (100-P)}{V_o \times F} \qquad (20)$$

where

E is the emission rate in kg/day

V_o is the volume of water/time containing E
(For example, discharge flow of sewage treatment plant).
If no other data are known, V_o should be based on the average sewage flow of a 10,000 population = 2000 m^3/day
(Average sewage flow: 150-200 l/capita and day)

P is the percentage removed from aqueous phase by degradation, adsorption on sludge or volatilization in a biological sewage treatment plant

The term 10 x 100 refers to the transformation kg/m^3 to mg/l

F is so-called dilution factor, derived from the ratio:
effluent discharge flow / (receiving water flow + discharge flow)

It should be noted, that this approach assumes immediate mixing after the discharge, which might be realistic only in the case of very turbulent water.

Dilution factor

Dilution factors have been reported to have values from 1 (e.g. No immediate mixing, dry riverbeds) to 100,000 *(RIVM report 6702080-01).*

Ispra table for determination of the removal rate

The removal rates P are suggested to be estimated on the basis of phys. chem. properties and the results of readily biodegradation tests from the Ispra WWTP removal rate table as in Table 7.

Table 7 has been based upon the results obtained within a Dutch project on modelling the elimination on chemicals in sewage treatment plants *(RIVM report 718703001).*

It can be seen that the Ispra table provides us a useful tool to estimate the removal rate of a chemical in a WWTP, when there is no data available. However, the reliability of this table remains to be further validated.

The results obtained from DRANC, STP, and Fugacity I are listed together with the values suggested in the Ispra table in Table 8. Then, a interesting phenomenon appears.

Table 7. The Ispra WWTP removal rate (P) table				
log Pow	Ready biodegradation	log H (Pa m^3/mol)	P %	Type
< 3	no	< 2	10	1
	yes	< 2	60	2
	no	2 - 3	60	3
	yes	2 - 3	80	4
	-	> 3	90	5
3 -5	no	< 2	60	6
	yes	< 2	80	7
	-	2 - 3	80	8
	-	> 3	95	9
> 5	-	-	90	10

The Ispra table agrees very well with all the three models for compounds of type 9 (logPow=3-5, logH>3) and type 10 (logPow>5).

But, the Ispra table greatly overestimates the removal rates for compounds of type 1 (logPow<3, logH<2, not ready biodegradable). In this case, the simplest model, Fugacity I, matches the Ispra table much better than DRANC and STP models.

For compounds of type 7 (logPow=3-5, logH<2, ready biodegradable), the results are diverse from each other. Both compound no.6 and compound no.11 are of type 7 according to the Ispra table. The Ispra table very much overestimates the removal rates compared to STP and Fugacity I models. However, the Ispra table underestimates the removal rate for compound no.6 , but overestimates the value for compound no.11, compared to DRANC model.

Some modifications are to be carried out for the Ispra table

Since this is just a very rough check of the Ispra table, no firm conclusion should be drawn yet. However, it might be suggested that more systematic validation should be carried out before the table is relied upon too much for calculating the PECs of chemicals which are treated in WWTP.

Table 8. Check the Ispra Table

Compound No.	Log Pow	Water Solubility, mg/l	LogH, Pa • m^3/mol	Ready Biodegradation	P% DRANC	P% STP	P% Fugacity I	P% Table
1	5.72	$6.6x10^{-3}$	0.6428	yes	95.1	99.46	98.79	90 (10*)
2	4.01	32	2.3334	no	88	59.25	89.7	80 (8)
3	6.1	6.4	0.2352 (low VP) 0.7666 (high VP)	no	94.5 94.6	92.58 92.59	99.48 99.49	90 (10) 90 (10)
4	7.3	$1.9x10^{-3}$	0.5205	no	95.1	93.98	99.97	90 (10)
5	1.09	214000	-0.8809	no	0.5	2.18	4.59	10 (1)
6	3.27	51	-0.5616	yes	91.2	11.77	27.60	80 (7)
7	0.73	188000	-0.5809	no	0.8	2.04	8.53	10 (1)
8	2.8	0.69	-1.9353	no	5.1	4.35	9.14	10 (1)
9	0.78	670000	-3.5900	yes	90.4	3.23	1.0	60 (2)
10	3.8	20	3.1733	no	95	86.97	99.81	95 (9)
11	3.5	3.11	-4.3113	yes	21.3	13.98	32.59	80 (7)
12	2.46	390	-0.3524	no	3.7	3.26	16.69	10 (1)

* Number of the type in the Ispra Table.

6 Discussion and conclusions

As it may be seen from above, validation of various existing models and systems is urgently needed in order to ensure the sound scientific basis of risk assessment.

How to validate a model

The validation of a model is, in general, a comparison between calculated and measured values. It is shown that the risk assessment system consists of four main parts: emission assessment, distribution modules, effect extrapolation and the calculation of risk quotients. When the risk assessment is carried out for new chemicals, the purpose is to characterise the risk of chemicals before they enter the market. Measured data for comparison with model results are not available. A validation of the risk assessment for new chemicals cannot therefore be carried out in general.

Thus, the best way to validate a part of the risk assessment system seems to validate the different distribution modules of the system separately, using measured input values, and comparing the output values with measured data.

Reasonable worst-case approach is preferred

It should be noted that the use of only worst-case assumptions in the scenarios can be misleading since the aim of the exposure analysis is to evaluate a chemical considering its entire life cycle and not only a particular situation. So, scenarios must be defined taking into account difficult but not unrealistic situations. "Reasonable worst-case" approach is associated with the choice of each of the necessary parameters: They could be mean, medium, 95% percent or absolute worst-case values. The values in these different situations may vary several magnitudes. Among others, the choice of an appropriate dilution factor is a typical example, which may vary from 1 to 100,000.

Important future task

Therefore, it is an essentially important task in the near future that, to strengthen the risk assessment expert group and construct our own risk assessment systems in order to use data input filling the specific environmental conditions in Denmark.

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APPENDIX A. Calculation of LogKow from the Original UNIFAC

Chemicals	logKow (exp.)	logKow (cal.)	(exp.-cal.)	Ref.
o-toluidine	1,29	1,2915	-0,0015	a
n-butylbenzene	4,28	4,2832	-0,0032	b
butanol	0,88	0,8924	-0,0124	c
2-pentanone	0,91	0,8946	0,0154	c
pyridine	0,65	0,6664	-0,0164	c
1,1,1-trichloroethane	2,49	2,4689	0,0211	c
n-pentane	2,50	2,4690	0,0310	d
1-octene	3,70	3,7378	-0,0378	e
2-heptene	3,20	3,2711	-0,0711	e
triethylamine	1,45	1,5319	-0,0819	c
n-hexane	3,00	2,9159	0,0841	e
diethyl ether	0,89	0,7884	0,1016	c
chloroform	1,97	2,0754	-0,1054	c
nitrobenzene	1,85	1,9583	-0,1083	c
m-toluidine	1,40	1,2915	0,1085	f
1,3-butadiene	1,99	1,8781	0,1119	c
3-methylpentane	2,80	2,9168	-0,1168	e
2-methylpentane	2,80	2,9168	-0,1168	e
isopropylbenzene	3,66	3,7834	-0,1234	e
acetophenone	1,58	1,7102	-0,1302	c
dimethylformamide	-1,01	-0,8762	-0,1338	c
n-heptane	3,50	3,3629	0,1371	e
4-methylpyridine	1,22	1,3572	-0,1372	c
1-hexene	2,70	2,8439	-0,1439	e
ethyl acetate	0,73	0,8811	-0,1511	c
n-propylbenzene	3,68	3,8363	-0,1563	e
2-methylbutane	2,30	2,4698	-0,1698	e
n-pentylbenzene	4,90	4,7302	0,1698	b
2-pentene	2,20	2,3772	-0,1772	e
n-octane	4,00	3,8098	0,1902	e
carbon tetrachloride	2,83	3,0226	-0,1926	c
2,4-dimethylphenol	2,30	2,4933	-0,1933	c
1-pentene	2,20	2,3970	-0,1970	e
nitromethane	-0,35	-0,1431	-0,2069	c
chlorobenzene (CB)	2,98	3,1902	-0,2102	b

Chemicals	logKow (exp.)	logKow (cal.)	(exp.-cal.)	Ref.
cyclopentane	2,05	2,2709	-0,2209	e
1,2-dichloroethane	1,48	1,7011	-0,2211	c
benzene	2,13	2,3578	-0,2278	c
1,4-cyclohexadiene	2,30	2,5343	-0,2343	c
ethylbenzene	3,15	3,3893	-0,2393	c
1-chlorobutane	2,55	2,3085	0,2415	g
3-pentanone	0,99	1,2319	-0,2419	c
hexanol	2,03	1,7863	0,2437	c
aniline	0,90	0,6539	0,2461	c
methyl acetate	0,18	0,4341	-0,2541	c
cyclohexane	2,46	2,7175	-0,2575	e
styrene	2,95	3,2110	-0,2610	c
2,4-dimethylpentane	3,10	3,3645	-0,2645	e
toluene	2,73	2,9954	-0,2654	c
2-butanol	0,61	0,8932	-0,2832	c
octanol	2,97	2,6802	0,2898	c
anisole	2,11	1,8201	0,2899	a
cycloheptane	2,87	3,1648	-0,2948	e
2-methylnaphthalene	4,11	4,4077	-0,2977	g
decane	5,01	4,7037	0,3063	h
decane	5,01	4,7037	0,3063	b
1,6-heptadiene	2,90	3,2189	-0,3189	e
hexachloroethane	4,14	3,8096	0,3304	i
cyclooctane	3,28	3,6117	-0,3317	e
heptanol	2,57	2,2332	0,3368	c
methylene chloride	1,25	1,5889	-0,3389	c
benzylamine	1,09	1,4295	-0,3395	c
n-hexylbenzene	5,52	5,1771	0,3429	b
chlorobenzene	2,84	3,1902	-0,3502	c
hexanoic acid	1,92	1,5640	0,3560	c
cyclohexanol	1,23	1,5890	-0,3590	c
1,3,5-trichlorobenzene	4,49	4,8549	-0,3649	c
methylcyclopentane	2,35	2,7187	-0,3687	e
pentachlorophenol	5,01	5,3798	-0,3698	j
dibutylamine	2,83	2,4439	0,3861	c
m-chloroaniline	1,88	1,4862	0,3938	g
2-propanol	0,05	0,4463	-0,3963	c

Chemicals	logKow (exp.)	logKow (cal.)	(exp.-cal.)	Ref.
1-ethylnaphthalene	4,39	4,8016	-0,4116	b
2-monochloronaphthalene	4,19	4,6024	-0,4124	a
o-chloroaniline	1,90	1,4862	0,4138	g
1,5-hexadiene	2,40	2,8208	-0,4208	e
1,3-dichlorobenzene	3,60	4,0225	-0,4225	c
1,4-pentadiene	1,90	2,3250	-0,4250	e
3-chlorobiphenyl	4,95	5,3763	-0,4263	g
cyclopentene	1,75	2,1791	-0,4291	e
m-xylene	3,20	3,6330	-0,4330	g
cyclohexene	2,16	2,6261	-0,4661	e
naphthalene	3,30	3,7701	-0,4701	c
fluorene	4,38	4,8554	-0,4754	j
p-dichlorobenzene	3,53	4,0225	-0,4925	j
2-butanone	0,29	0,7850	-0,4950	c
1-ethyl-2-methylbenzene	3,53	4,0269	-0,4969	b
1-chloroheptane	4,15	3,6494	0,5006	b
C12H26	6,10	5,5976	0,5024	b
cycloheptene	2,57	3,0730	-0,5030	e
2-methyl-2-propanol	0,35	0,8602	-0,5102	c
dimethyl sulfoxide	-1,35	-1,8633	0,5133	c
1-methylnaphthalene	3,87	4,4077	-0,5377	b
2-methylnaphthalene	3,86	4,4077	-0,5477	b
1,2-dimethylcyclohexane	3,06	3,6134	-0,5534	e
1,4-dichloronaphthalene	4,88	5,4348	-0,5548	a
1,1,2,2-tetrachloroethane	2,39	2,9613	-0,5713	c
fluoranthene	5,22	5,8207	-0,6007	b
2,7-dichloronaphthalene	4,81	5,4348	-0,6248	a
1,2,4-trichlorobenzene	4,23	4,8548	-0,6248	j
1,3-dimethylnaphthalene	4,42	5,0453	-0,6253	b
4,4'-PCB	5,58	6,2086	-0,6286	i
1,4-dichlorobenzene	3,38	4,0225	-0,6425	a
1,2-CB	3,38	4,0225	-0,6425	b
2,3-dimethylnaphthalene	4,40	5,0453	-0,6453	b
1,5-dimethylnaphthalene	4,38	5,0453	-0,6653	b
1,4-dimethylnaphthalene	4,37	5,0453	-0,6753	b
1,3,7-trichloronaphthalene	5,59	6,2671	-0,6771	a
p-cymene	4,10	4,7823	-0,6823	c

Chemicals	logKow (exp.)	logKow (cal.)	(exp.-cal.)	Ref.
methylcyclohexane	2,76	3,4431	-0,6831	e
3-methylcholanthrene	7,11	7,7941	-0,6841	c
1,2-benzoanthracene	5,91	6,5945	-0,6845	b
tetracene	5,90	6,5945	-0,6945	c
2,3-benzanthracene	5,90	6,5945	-0,6945	b
1-heptene	3,99	3,2909	0,6991	g
acetal	0,84	1,5414	-0,7014	c
C14H30	7,20	6,4915	0,7085	b
C14H30	7,20	6,4915	0,7085	i
1,3,5-trimethylbenzene	3,56	4,2707	-0,7107	c
benzyl alcohol	1,10	1,8127	-0,7127	a
1,3,5,7-tetrachloronaphthalene	6,38	7,0994	-0,7194	b
1,2,3-trimethylbenzene	3,55	4,2707	-0,7207	c
phenanthrene	4,46	5,1823	-0,7223	a
2,3-dichloronaphthalene	4,71	5,4348	-0,7248	c
anthracene	4,45	5,1823	-0,7323	b
perylene	6,50	7,2329	-0,7329	b
2,6-dimethylnaphthalene	4,31	5,0453	-0,7353	j
lindane	3,85	4,5934	-0,7434	a
benzaldehyde	1,48	2,2287	-0,7487	c
9-methylanthracene	5,07	5,8199	-0,7499	f
9-methylanthracene	5,07	5,8199	-0,7499	c
N-methylaniline	1,66	0,9005	0,7595	b
1,2,3,5-tetrachlorobenzene	4,92	5,6872	-0,7672	c
1,4,5-trimethylnaphthalene	4,90	5,6829	-0,7829	b
p-xylene	3,15	3,9371	-0,7871	c
2,3-benzofluorene	5,75	6,5387	-0,7887	b
1-methylfluorene	4,97	5,7640	-0,7940	b
chrysene	5,79	6,5945	-0,8045	b
3,5-dichlorobiphenyl	5,40	6,2086	-0,8086	a
1,2,3-trichlorobenzene	4,04	4,8549	-0,8149	a
1,2:3,4-dibenzanthracene	7,19	8,0068	-0,8168	b
2,3:6,7-dibenzanthracene	7,19	8,0068	-0,8168	b
1,2:5,6-dibenzanthracene	7,19	8,0068	-0,8168	b
2-chlorobiphenyl	4,54	5,3763	-0,8363	g
1,2-diphenylethane	4,79	5,6505	-0,8605	e
o-xylene	2,77	3,6330	-0,8630	g

Chemicals	logKow (exp.)	logKow (cal.)	(exp.-cal.)	Ref.
3,4-benzopyrene	5,98	6,8460	-0,8660	b
2-PCB	4,51	5,3764	-0,8664	i
3,3′-dichlorobiphenyl	5,30	6,2086	-0,9086	a
2-chlorophenanbthrene	5,16	6,0850	-0,9250	j
benzo[a]pyrene	5,97	6,9137	-0,9437	c
diphenylmethane	4,14	5,0972	-0,9572	e
2-methylphenanthrene	4,86	5,8199	-0,9599	j
1-nonene	5,15	4,1848	0,9652	g
1,2,4,5-tetrachlorobenzene	4,70	5,6872	-0,9872	i
2,4,5-trichlorophenol	2,72	3,7151	-0,9951	j
pyrene	4,80	5,8207	-1,0207	c
1,8-dichloronaphthalene	4,41	5,4348	-1,0248	a
2,4′-dichlorobiphenyl	5,14	6,2086	-1,0686	c
1,2,3,4-tetrachlorobenzene	4,60	5,6872	-1,0872	i
2,4′-PCB	5,10	6,2086	-1,1086	i
2,5-dichlorobiphenyl	5,10	6,2086	-1,1086	a
4-chlorobiphenyl	4,26	5,3763	-1,1163	j
tetrahydrofuran	0,46	-0,6751	1,1351	c
1,3,5,8-tetrachloronaphthalene	5,96	7,0994	-1,1394	a
1,2,3,4-tetrachloronaphthalene	5,94	7,0994	-1,1594	a
9,10-dimethlanthracene	5,25	6,4575	-1,2075	b
1,2-benzofluorene	5,32	6,5387	-1,2187	b
2,3-dichlorobiphenyl	4,97	6,2086	-1,2386	a
N,N-dimethylaniline	2,31	1,0573	1,2527	f
2,2′-dichlorobiphenyl	4,90	6,2086	-1,3086	a
acenaphthene	3,92	5,2414	-1,3214	c
2,5,4′-trichlorobiphenyl	5,70	7,0410	-1,3410	a
4-methyl-1-pentene	2,50	3,8448	-1,3448	e
2,2′-PCB	4,80	6,2086	-1,4086	i
2,4,4′-PCB	5,62	7,0411	-1,4211	i
biphenyl	4,04	2,6092	1,4308	c
benz[a]anthracene	5,61	7,0493	-1,4393	j
2,5,2′-trichlorobiphenyl	5,60	7,0410	-1,4410	a
2,2′,5-trichlorobiphenyl	5,60	7,0410	-1,4410	a
methoxychlor	4,30	5,7565	-1,4565	j
penta-CB	5,03	6,5195	-1,4895	b
tert-butylbenzene	4,11	2,5411	1,5689	g

Chemicals	logKow (exp.)	logKow (cal.)	(exp.-cal.)	Ref.
2,5,3',5'-tetrachlorobiphenyl	6,26	7,8733	-1,6133	a
chlordane	6,00	7,7077	-1,7077	j
2,5,2',5'-tetrachlorobiphenyl	6,10	7,8733	-1,7733	a
3,4,3',4-tetrachlorobiphenyl	6,10	7,8733	-1,7733	a
2,2',5,5'-tetrachlorobiphenyl	6,09	7,8733	-1,7833	c
2,2',4,4',5,5'-hexaphenyl	7,75	9,5373	-1,7873	c
hexa-CB	5,47	7,3519	-1,8819	b
p-cymene	6,34	4,4214	1,9186	i
2,3',4',5-tetrachlorobiphenyl	5,90	7,8733	-1,9733	a
2,3,4,5-tetrachlorobiphenyl	5,90	7,8733	-1,9733	a
2,2',4,4',6,6'-hexaphenyl	7,55	9,5373	-1,9873	c
2,3,5,6-tetrachlorobiphenyl	5,86	7,8733	-2,0133	a
hexachlorobenzene	5,31	7,3519	-2,0419	c
2,5,2',5'-PCB	5,81	7,8735	-2,0635	i
7,12-dimethylbenz[a]anthracene	5,80	7,8698	-2,0698	c
2,4,3',4'-tetrachlorobiphenyl	5,80	7,8733	-2,0733	a
p-nitrophenol	2,91	0,8185	2,0915	j
2,2',3,4,4'-pentachlorobiphenyl	6,61	8,7057	-2,0957	c
2,3,2',4-tetrachlorobiphenyl	5,76	7,8733	-2,1133	a
2,4,6,3',4'-pentachlorobiphenyl	6,58	8,7057	-2,1257	a
2,2',3,5',6-pentachlorobiphenyl	6,55	8,7057	-2,1557	c
2,3,4,2',5'-pentachlorobiphenyl	6,50	8,7057	-2,2057	a
dibenz[a,h]anthracene	5,80	8,0068	-2,2068	c
2,5,2',6'-tetrachlorobiphenyl	5,62	7,8733	-2,2533	a
2,3,2',3'-tetrachlorobiphenyl	5,60	7,8733	-2,2733	a
2,4,5,2',5'-pentachlorobiphenyl	6,40	8,7057	-2,3057	a
2,2',3,4,5'-pentachlorobiphenyl	6,37	8,7057	-2,3357	c
pentachlorobenzene	5,17	7,5195	-2,3495	c
2,3,4,5,3',4'-hexachlorobiphenyly	7,18	9,5380	-2,3580	a
o-dichlorobenzene	6,42	4,0225	2,3975	f
2,3,4,5,6-pentachlorobiphenyl	6,30	8,7057	-2,4057	a
2,4,6,2',5'-pentachlorobiphenyl	6,22	8,7057	-2,4857	a
2,4,6,2',4',6'-hexachlorobiphenyl	7,00	9,5380	-2,5380	a
o,p'-DDT	5,75	8,3064	-2,5564	j
2,2',3,3',4,4'-hexaphenyl	6,96	9,5373	-2,5773	c
2,4,5,2',5'-PCB	6,11	8,7063	-2,5963	i
2,4,5,2',4',5'-hexachlorobiphenyl	6,90	9,5380	-2,6380	a

Chemicals	logKow (exp.)	logKow (cal.)	(exp.-cal.)	Ref.
2,2′,4,4′,5,5′-hexachlorobiphenyl	6,90	9,5380	-2,6380	a
2,3,4,5,2′,5′-hexachlorobiphenyl	6,82	9,5380	-2,7180	a
p,p′-DDT	5,75	8,4966	-2,7466	j
2,3,4,2′,3,′,4′-hexachlorobiphenyl	6,74	9,5380	-2,7980	a
2,4,5,2′,4′,5′-PCB	6,72	9,5373	-2,8173	i
2,3,4,6,2′,4′-hexachlorobiphenyl	6,67	9,5380	-2,8680	a
2,4,6,2′,6′-pentachlorobiphenyl	5,81	8,7057	-2,8957	a
2-ethylhexylphthalate	4,20	7,3150	-3,1150	j
2,2′,3,3′,4,4′,6-heptachlorobiphenyl	6,68	10,3718	-3,6918	c
2,2′,3,3′,4′,5,5′,6,6′-nonachlorobiphenyl	8,16	12,0356	-3,8756	c
2,3,4,5,2′,3′,4′,5′-octachlorobiphenyl	7,10	11,2027	-4,1027	a
2,2′,3,3′,4,4′,5,5′-octachlorobiphenyl	7,10	11,2027	-4,1027	a
decachlorobiphenyl	8,26	12,8630	-4,6030	c
2,4-dimethylphenol	7,23	2,4933	4,7367	f
2,3,4,5,6,2′,3′,4′,5′-nonachlorobiphenyl	7,20	12,0350	-4,8350	a
Average absolute error = 0.9872				

* a. Clark,K.E. et al. (1990). b. Miller,M.M. and Wasik,S.P. (1985). c. Mackay,D. (1982).

d. Stefan et al. (1990). e. Kier,L.B. and Hall,L.H. (1976). f. Banerjee,S. et al. (1990).

g. Chiou,C.T. and Schmedding,D.W. (1982). h. Coates,M. et al. (1985). i. Chiou,C.T. (1985).

j. Banerjee,S. and Howard,P.H. (1988).

Appendix B Comparison of LogKow calculations

Chemicals	logKow(exp.)	The New Parameter Table		The Original Parameter Table	
		logKow (cal.)	abs.dev.	logKow (cal.)	abs.dev.
hexabromobiphenyl[a]	6,39	5,09	1,30	68,82	62,43
mirex[a]	6,89	7,35	0,46	7,57	0,68
hexabromocyclododecane[a]	5,81	6,29	0,48	75,87	70,06
5-bromoindole[a]	2,97	1,75	1,22	13,16	10,19
2,4,6-tribromoanisole[a]	4,48	2,09	2,39	38,59	34,11
1-pentyne[b]	1,98	1,86	0,11	15,67	13,69
1-hexyne[b]	2,48	2,52	0,043	16,11	13,63
1-heptyne[b]	2,98	3,18	0,20	16,56	13,58
1-octyne[b]	3,48	3,84	0,36	17,01	13,53
1-nonyne[b]	3,98	4,50	0,52	17,46	13,48
1,8-nonadiyne[b]	3,46	2,60	0,86	30,66	27,20
1,6-heptadiyne[b]	2,46	1,28	1,18	29,76	27,30
1,4-dibromobenzene[c]	3,89	2,52	1,37	23,78	19,89
1,3,5-tribromobenzene[c]	5,26	2,62	2,63	34,50	29,24
4,4'-dibromobiphenyl[c]	5,72	4,67	1,04	25,97	20,25
2,4,6-tribromobiphenyl[d]	6,03	4,78	1,25	36,68	30,65
2,2',5,5'-tetrabromobiphenyl[d]	6,50	4,88	1,62	47,40	40,90
2,2',4,4',6,6'-hexabromobiphenyl[d]	7,20	5,09	2,11	68,82	61,62
bromobenzene[e]	3,12	2,42	0,70	13,07	9,95
p-cymene[e]	6,34	5,57	0,77	4,42	1,92
tert-butylbenzene[f]	4,11	5,10	0,99	2,54	1,57
1-bromobutane[g]	2,75	3,05	0,30	12,70	9,95
1-bromopentane[g]	3,37	3,71	0,34	13,15	9,78
1-bromohexane[g]	3,80	4,37	0,57	13,60	9,80
1-bromoheptane[g]	4,36	5,03	0,67	14,04	9,68
1-bromooctane[g]	4,89	5,68	0,80	14,49	9,60
bromochloromethane[g]	1,41	1,00	0,41	11,64	10,24
1-bromo-3-chloropropane[g]	2,18	2,32	0,14	12,54	10,36
4-bromo-1-butane[g]	2,53	3,05	0,52	12,70	10,17
allyl bromide[g]	1,79	1,78	0,0048	12,18	10,39

* a. Banerjee,S. and Howard,P.H. (1988). b. Kier,L.B. and Hall,L.H. (1976). c. Stefan et al. (1990). d. Clark,K.E. et al. (1990). e. Chiou,C.T. (1985). f. Chiou,C.T. and Schmedding,D.W. (1982). g. Miller,M.M. and Wasik,S.P. (1985).

Appendix C MANUAL FOR PROGRAM *GAMMA*

Background

The UNIFAC group-contribution method is a well-known Danish model parallel to QSARs (Fredenslund et al. 1975, 1977). It was developed for chemical engineering purposes, has been widely applied in many areas of chemical engineering, and has been proven to be a fast and reliable tool for predicting liquid-phase activity coefficients. The UNIFAC model is based on the group-contribution concept. The basic idea of the group-contribution method is that compounds may be structurally decomposed into functional groups (for instance, all the linear alkanes contains only CH_3 and CH_2 groups), each having a unique contribution toward the compound property. The attractive aspect of this approach is that whereas there are thousands of chemical compounds of interest in commerical use, the number of functional groups which constitute these compounds is much smaller. Therefore, if we assume that a physical property of a fluid is the sum of contributions made by the molecules' functional groups, we obtain a possible technique to utilize existing experimental data for predicting the properties of systems for which no experimental data are available.

Activity coefficients represent the non-ideal behavior of a solution. By virtue of the activity coefficient, the UNIFAC model can be applied to describe many environmentally important properties, among those are 1-octanol/water partition coefficient, water solubility, and the Henry's law constant.

In the UNIFAC model, the activity coefficient for molecule i is calculated from two parts:

$$\ln\gamma_i = \ln\gamma_i^C + \ln\gamma_i^R \qquad \text{(M-1)}$$

where γ_i is the activity coefficient for the component i, γ_i^C is the combinatorial part, and γ_i^R is the residual part. The combinatorial term takes into account entropy effects and depends on the size and the shape of molecule i. In the combinatorial part, the group surface volume and area for each functional group are used as model parameters. These are determined using the compilation by Bondi (1968) and presented in Table M-1 as R_K and Q_K. The residual term is mainly governed by the energetic interactions of different groups of molecules. The group-interaction parameter, a_{mn} and a_{nm}, are introduced in this term. Reliable experimental binary vapor-liquid equilibrium data for representive systems are required to determine the group-interaction parameters.

There is a very important, so-called Gibbs-Duhem equation in thermodynamics. The Gibbs-Duhem equation interrelates activity coefficients of all components in a mixture. Therefore, if data are available for all of the activity coefficients, these data should obey the Gibbs-Duhem equation; if they do not, then the data cannot be correct. This lay the foundation of thermodynamic consistency test (Christiansen and Fredenslund, 1975). All the vapor-liquid equilibrium data used to determine UNIFAC group-interaction parameters have passed the thermodynamic consistency test.

In 1977, an extensive UNIFAC parameter table was published by Fredenslund et al. (1977). This parameter table has been revised and extended in a series of articles. Recently, the fifth version has been completed (Hansen et al., 1991). In this new version, a total of 223 pairs of group-interaction parameters have been revised or added to the parameter table. Six new main group have been added, such that UNIFAC has been extended to cover mixtures with chlorofluorohydrocarbons, amides, glycol ethers, sulfides, morpholine, and thiophenes. Based on the fifth version of the UNIFAC group-interaction parameters, the applicability of the UNIFAC model for environmental purpose has been evaluated, and a new set of group-interaction parameters has been developed for highly hydrophobic systems (Chen et al., 1992).

The UNIFAC Model

The combinatorial part of Eq. M-1 is given for a binary mixture by

$$\ln\gamma_1^C = \ln\frac{\varphi_1}{x_1} + \frac{z}{2}q_1\ln\frac{\theta_1}{\varphi_1} + l_1 - \frac{\varphi_1}{x_1}(x_1 l_1 + x_2 l_2) \qquad \text{(M-2)}$$

and

$$\ln\gamma_2^C = \ln\frac{\varphi_2}{x_2} + \frac{z}{2}q_2\ln\frac{\theta_2}{\varphi_2} + l_2 - \frac{\varphi_2}{x_2}(x_1 l_1 + x_2 l_2) \qquad \text{(M-3)}$$

where

$$\varphi_1 = \frac{r_1 x_1}{r_1 x_1 + r_2 x_2} \qquad \theta_1 = \frac{q_1 x_1}{q_1 x_1 + q_2 x_2} \qquad \text{(M-4)}$$

$$\varphi_2 = \frac{r_2 x_2}{r_1 x_1 + r_2 x_2} \qquad \theta_2 = \frac{q_2 x_2}{q_1 x_1 + q_2 x_2} \qquad \text{(M-5)}$$

Note that $\varphi_1 + \varphi_2 = 1$ and $\theta_1 + \theta_2 = 1$.

$$l_1 = \frac{z}{2}(r_1 - q_1) - (r_1 - 1); \qquad z = 10 \qquad \text{(M-6)}$$

$$l_2 = \frac{z}{2}(r_2-q_2)-(r_2-1)$$

$$r_1 = \sum_k \nu_k^{(1)} R_k \ ; \qquad r_2 = \sum_k \nu_k^{(2)} R_k \tag{M-7}$$

$$q_1 = \sum_k \nu_k^{(1)} Q_k \ ; \qquad q_2 = \sum_k \nu_k^{(2)} Q_k$$

and where

x_1, x_2 = mole fraction of components 1 and 2
ν_k = 1,2,....N (number of groups in molecule 1 or 2)
R_k = the van der Waals volume for group k
Q_k = the van der Waals surface area for group k
k = group number (assigned)

In Table M-1 group volumes and surface areas are given for 50 main groups for the original UNIFAC model. Table M-3 represents values for 31 main groups that have been studied up to date.

For a binary mixture, the residual part of Eq. M-1 is given by:

$$\ln\gamma_1^R = \sum_k \nu^{(1)}(\ln\Gamma_k - \ln\Gamma_k^{(1)}) \tag{M-8}$$

$$\ln\gamma_2^R = \sum_k \nu^{(2)}(\ln\Gamma_k - \ln\Gamma_k^{(2)})$$

where

$$\ln\Gamma_k = Q_k(1-\ln(\sum_m \Theta_m \Psi_{mk}) - \sum_m (\Theta_m \Psi_{mk} / \sum_n \Theta_n \Psi_{nm}))$$

and m and n = 1,2,....,N (all groups)

$$\Theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n} \qquad X_m = \frac{\sum_j \nu_m^{(j)} x_j}{\sum_j \sum_n \nu_n^{(j)} x_j} \tag{M-10}$$

j = 1,2,..., M; n = 1,2,..., N

Similar relationships hold for $\ln\Gamma_k^{(1)}$ and $\ln\Gamma_k^{(2)}$. Note, however, that these refer to the pure components.

Furthermore,

j = component number (1 or 2 for a binary mixture)
M = total number of components (=2 for a binary mixture)
n = group number
N = total groups
Θ_m = group surface area fraction
X_m = group fraction (For example, for an equimolar mixture of butane and hexane, the group fraction for CH_3 and CH_2 are 4/10 and 6/10, respectively.)
x_j = mole fraction of molecule j in the mixture
$v_m^{(j)}$ = number of groups of type m in molecule j
Ψ_{nm} = $\exp(-a_{nm}/T)$ (M-11)
T = temperature (K)

The parameter a_{nm} is the group interaction parameters. The interaction parameters for the 50 main groups and the 31 main groups are listed in Tables M-2 and M-4, respectively.

Basic Steps

(1) Draw the structrues of the chemicals involved.
(2) Determine the kind and number of structural groups corresponding to those represented in Table M-1 or M-3.
(3) Calculate r_1, r_2, q_1 and q_2 using Eq. M-7 and the R_k and Q_k values from Table 1.
(4) Calculate l_1 and l_2 from Eq. M-6.
(5) Calculate Φ_1, Φ_2, θ_1 and θ_2 from Eq. M-5.
(6) Calculate $\ln\gamma_1^C$ and $\ln\gamma_2^C$ from Eqs. M-2 and M-3.
(7) Calculate Θ_m and X_m for each group, using Eq. M-10. Note that $\Sigma\Theta_m = \Sigma X_m = 1$.
(8) Calculate Ψ_{mn} for each group using the value of a_{mn} in Appendix B and Eq. M-11. Note that m and n are subgroup numbers.
(9) Calculate $\ln\Gamma_k$ and $\ln\Gamma_k^{(j)}$ for each group, using Eq. M-9.
(10) Calculate $\ln\gamma_1^R$ and $\ln\gamma 2^R$ using Eq. M-8.
(11) Calculate $\ln\gamma 1$ and $\ln\gamma 2$ using Eq. M-1.

Program *GAMMA*

GAMMA calculates activity coefficients in liquid mixtures by means of the following model:

1) UNIFAC with built-in original VLE parameters
2) UNIFAC with built-in new parameters for highly hydrophobic systems (water parameter)

Some or all of the built-in UNIFAC-parameters may be substituted externally.

The program is written in FORTRAN 77 language and can be used on any MS-DOS computer. The following procedures may be used to install *GAMMA* on the hard disk of your PC:

- Create a new directory C:\GAMMA on drive C.
  Just type **md GAMMA <enter>**.
- Copy all the files from diskette to the directory C:\GAMMA.
  Just insert the diskette to your drive A:, type **copy a:*.* <enter>**.

Then, after the input specification has been given as follows, program *GAMMA* can be run from the directory C:\GAMMA by typing **GAMMA <enter>**.

Input specification

line 1: NTEXT: any text

line 2: MODEL, IOUT, NFIL

MODEL=1: UNIFAC (original-VLE)

MODEL=2: UNIFAC (water parameter)

IOUT=0: output only on file "gamma.out"

IOUT=1: output on screen and file "gamma.out"

line 2a: IFIL1, IFIL6 (only if NFIL≠0)

IFIL1: unit number for output-file

IFIL6: unit number for screen

line 3: NC

NC: number of components (max. =10)

The next input cards are for subroutine MODIN. A specific description will follow later on. After this follows:

line 4: T

T: temperature in Kelvin

1(2) card(s): (X(I), I=1,NC)

X(I): mole fraction of component I[*]

At termination of a run, a new temperature and a set of mole fractions may be entered. A session is terminated by line "0.0".

---

[*] X(I)=0 should be used when the infinite dilution activity coefficient of component I is calculated.

MODIN

Input routine for UNIFAC. MODIN accesses data files of parameters for the UNIFAC (original-VLE) method and the UNIFAC (water parameter) method.

Tables M-1 and M-2 at the end of this manual show group definitions, R and Q values and group interaction parameters for the UNIFAC methed with original-VLE parameters (Hansen et al., 1991). Tables M-3 and M-4 show parameters for the UNIFAC method with new parameters for highly hydrophobic systems (Chen et al., 1992).

The UNIFAC parameter tables are given in the files

UNIPAR.X80	UNIFAC (original-VLE) parameter table
WATPAR.X80	UNIFAC (water parameter) parameter table

Arguments: NC, NG, MODEL, IOUT, IFIL1

NC, MODEL, IOUT must be specified in the calling program as described above. NG is an output variable from the subroutine.

Input Data for the Subroutine MODIN

line 1: ISPEC

ISPEC=0: UNIFAC R and Q parameters are retrieved from internal data files.

ISPEC>0: Number of user specified subgroups.

line 2
(k lines): (Only if ISPEC>0)IDK, SGNAME, IDMG, RG, QG

IDK: Number of the subgroup for which the user specifies his own R and Q values. The subgroup numbers must be in accordance with the numbers used in table M-1 or M-3.

SGNAME: An identification text for this subgroup.

IDMG: Number of the corresponding main group.

RG: UNIFAC R value for this subgroup.

QG: UNIFAC Q value for this subgroup.

next k lines: (NY(K), IDENT(K), K=1,7)

Specification of types and numbers of the different subgroups contained in each component.

NY: Number of times that the subgroup IDENT appears in the component.

IDENT: Number of the k-th subgroup in the component. The subgroups in each component must be specified in the same order as they appear in table 1, starting with the subgroup which has the lowest number.

next line: ISPEC2

ISPEC2=0: UNIFAC group interaction parameters are read from internal file.

ISPEC2>0: Number of user specified interaction parameters.

next k lines: (Only if ISPEC2>0) I, J, PNEW

I,J: Number of the main group.

PNEW: UNIFAC user specified value for the interaction $(u_{ij}-u_{jj})/R$.

Input Example

For a mixture of water (1), ethanol (2), and benzene (3) to be calculated by the UNIFAC method with original-VLE with built-in parameters

```
0

1  17

1  1  1  2  1  15

6  10

0
```

References

Chen,F., Holten-Andersen,J. and Tyle,H., "New developments of the UNIFAC model for environmental application", submitted to *Chemosphere*, 1992.

Christiansen,L.J. and Fredenslund,Aa., *AICHE J*. 21, 49, 1975.

Fredenslund,Aa., Jones,R.L., and Prausnitz,J.M., *AICHE J*. 21, 1086, 1975.

Fredenslund, Aa., Gmehling, J. and Rasmussen, P., "Vapor-liquid Equilibria Using UNIFAC", Elsevier 1977.

Hansen, H.K., Rasmussen, P., Fredenslund, Aa., Schiller, M. and Gmehling, J., "Vapor-Liquid Equilibria by UNIFAC Group Contribution: 5. Revision and Extension", Ind. Eng. Chem. Res. Vol.30, No.10, 2352, 1991.

Magnussen, T. "Description of A Library of Thermodynamic Subroutines", MAN 8101, Institut for Kemteknik, The Technical University of Denmark, 1981.

INPUT / OUTPUT FILE HANDLING

INPUT

All lines in the input file can be written in FREE FORMAT mode. After each line, type / (slash). For example

```
2 3 2 2 /
```

The / indicates end of line for READ statement.

Text lines have to be written in quotes. For example

```
' TEXT '
```

The user prepared input file will, in most cases, be READ on UNIT = 5.

OUTPUT

An output file, GAMMA.OUT will be created if IOUT=0. If IOUT=1, in addition to the GAMMA.OUT file, the OUTPUT will also be displayed on the screen.

In the default option, GAMMA.OUT is written on UNIT=IFIL1=1 and the screen display in made through UNIT=IFIL6=6. For computers (or complilers) which do not allow this, the values of IFIL1 AND IFIL6 need to be changed. This can be done through the variable NFIL. If NFIL=0, default values of IFIL1 and IFIL6 are used. If NFIL=1, th user must provide these values through line 2a.

Example 1

This input file "GAMMA.DAT" is assigned to calculate the infinite dilution activity coefficients of 2-methyl-1-butene (1) in water (2) phase and octanol (3) phase by using the UNIFAC (original-VLE) method.

INPUT EXAMPLE

```
’2-methyl-1-butene(1)-water(2)-octanol(3)’/
1  1  0           /
3                 /
0                 /
2  1  1  2  1  7    /
1  17              /
1  1  7  2  1  15   /
0                 /
298.              /
0.  1.  0.        /
298.              /
0.  0.  1.        /
0.0               /
```

OUTPUT EXAMPLE

```
1


 IOUT =  1
 IF IOUT = 0 : OUTPUT ONLY ON FILE
 IF IOUT = 1 : OUTPUT ON BOTH FILE AND SCREEN


 2-methyl-1-butene(1)-water(2)-octanol(3)



 MODEL USED FOR LIQUID PHASE: ORIGINAL UNIFAC   (VLE)


 GROUP SPECIFICATION:
```

```
SUBGROUP       MAIN       R        Q    PRESENCE IN COMPONENT NO.
NO.  NAME      GROUP                     1  2  3

 1  CH3.....    1     0.9011    0.8480  2  0  1
 2  CH2.....    1     0.6744    0.5400  1  0  7
 7  CH2=C...     2     1.1173    0.9880  1  0  0
15   OH......   5     1.0000    1.2000  0  0  1
17   H2O.....   7      0.9200    1.4000  0  1  0


PARAMETER COEFFICIENTS FOR INTERACTIONS

           1          2          5          7
 1
        0.0000      86.02      986.5      1318.
 2
        -35.36     0.0000      524.1      270.6
 5
         156.4      457.0     0.0000      353.5
 7
         300.0      496.1     -229.1     0.0000


MOLECULAR PARAMETERS

COMP.    R          Q

  1   3.5939    3.2240
  2   0.9200    1.4000
  3   6.6219    5.8280


TEMPERATURE:  298.000

 MOLE PER CENT    ACTIVITY COEFFICIENT
    0.000000          2327.69
  100.000000           1.00000
    0.000000          3171.00


TEMPERATURE:  298.000

 MOLE PER CENT    ACTIVITY COEFFICIENT
    0.000000          1.62153
    0.000000          5.77492
  100.000000           1.00000
```

Example 2

This input file "GAMMA.DAT" is assigned to calculate the infinite dilution activity coefficients of 1-hexyne (1) in water (2) phase and octanol (3) phase by using the UNIFAC (water parameter) method.

INPUT EXAMPLE

```
'1-hexyne(1)-water(2)-octanol(3)'/
2  1  0            /
3                  /
0                  /
1  1  3  2  1  59    /
1  17              /
1  1  7  2  1  15    /
0                  /
298.               /
0.  1.  0.         /
298.               /
0.  0.  1.         /
0.0                /
```

OUTPUT EXAMPLE

```
1


 IOUT =  1
 IF IOUT = 0 : OUTPUT ONLY ON FILE
 IF IOUT = 1 : OUTPUT ON BOTH FILE AND SCREEN


 1-hexyne(1)-water(2)-octanol(3)


 MODEL USED FOR LIQUID PHASE: ORIGINAL UNIFAC  (WATER)
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GROUP SPECIFICATION:

 SUBGROUP      MAIN      R        Q    PRESENCE IN COMPONENT NO.
 NO.  NAME     GROUP                      1  2  3

   1  CH3.....    1    0.9011    0.8480  1  0  1
   2  CH2.....    1    0.6744    0.5400  3  0  7
  15  OH......    5    1.0000    1.2000  0  0  1
  17  H2O.....    7    0.9200    1.4000  0  1  0
  59  CH=-C...   30    1.2920    1.0880  1  0  0


PARAMETER COEFFICIENTS FOR INTERACTIONS

           1          5          7          30
   1
        0.0000     986.5     -483.8      298.9
   5
         156.4     0.0000    -521.7      9999.
   7
         2076.     1317.     0.0000      63.79
  30
        -72.88     9999.      59.74      0.0000


MOLECULAR PARAMETERS

COMP.     R        Q

   1   4.2163   3.5560
   2   0.9200   1.4000
   3   6.6219   5.8280


TEMPERATURE:  298.000

 MOLE PER CENT     ACTIVITY COEFFICIENT
     0.000000          7272.71
   100.000000           1.00000
     0.000000          148568.


TEMPERATURE:  298.000

 MOLE PER CENT     ACTIVITY COEFFICIENT
     0.000000          3.28949
     0.000000         0.313924
   100.000000           1.00000
```

Tables M-1 to M-4

Table M-1

UNIFAC (original-VLE) Group Volume (Rk) and Surface Area (Qk) parameters

Main Group	Sub group	No.	R_k	Q_k	Sample Group Assignment	
1	CH_3	1	0.9011	0.848	Hexane :	2 CH_3, 4 CH_2
"CH_2"	CH_2	2	0.6744	0.540		
	CH	3	0.4469	0.228	2-Methylpropane :	3 CH_3, 1 CH
	C	4	0.2195	0.000	Neopentane :	4 CH_3, 1 C
2	CH_2=CH	5	1.3454	1.176	Hexene-1 :	1 CH_3, 3 CH_2, 1 CH_2=CH
"C=C"	CH=CH	6	1.1167	0.867	Hexene-2 :	2 CH_3, 2 CH_2, 1 CH=CH
	CH_2=C	7	1.1173	0.988	2-Methyl-1-butene :	2 CH_3, 1 CH_2, 1 CH_2=C
	CH=C	8	0.8886	0.676	2-Methyl-2-butene :	2 CH_3, 1 CH=C
	C=C	9	0.6605	0.485	2,3-Dimethylbutene :	4 CH_3, 1 C=C
3	ACH	10	0.5313	0.400	Naphthaline :	8 ACH, 2 AC
"ACH"	AC	11	0.3652	0.120	Styrene :	1 CH_2=CH, 5 ACH, 1 AC
4	$ACCH_3$	12	1.2663	0.968	Toluene :	5 ACH, 1 $ACCH_3$
"$ACCH_2$"	$ACCH_2$	13	1.0396	0.660	Ethylbenzene :	1 CH_3, 5 ACH, 1 $ACCH_2$
	ACCH	14	0.8121	0.348	Cumene :	2 CH_3, 5 ACH, 1 ACCH
5 "OH"	OH	15	1.0000	1.200	Propanol-2 :	2 CH_3, 1 CH, 1 OH
6 "CH_3OH	CH_3OH	16	1.4311	1.432	Methanol :	1 CH_3OH
7 "H_2O	H_2O	17	0.9200	1.400	Water :	1 H_2O
8 "ACOH"	ACOH	18	0.8952	0.680	Phenol :	5 ACH, 1 ACOH

Table M-1 (continued)

UNIFAC (original-VLE) Group Volume (Rk) and Surface Area (Qk) parameters

Main Group	Sub group	No.	R_k	Q_k	Sample Group Assignment	
9	CH_3CO	19	1.6724	1.448	Butanone :	1 CH_3, 1 CH_2, 1 CH_3CO
"CH_2CO"	CH_2CO	20	1.4457	1.180	Pentanone-3 :	2 CH_3, 1 CH_2, 1 CH_2CO
10 "CHO"	CHO	21	0.9980	0.948	Propionic aldehyde :	1 CH_3, 1 CH_2, 1 CHO
11	CH_3COO	22	1.9031	1.728	Butyl acetate :	1 CH_3, 3 CH_2, 1 CH_3COO
"CCOO"	CH_2COO	23	1.6764	1.420	Methyl propionate :	2 CH_3, 1 CH_2COO
12 "HCOO"	HCOO	24	1.2420	1.188	Ethyl formate :	1 CH_3, 1 CH_2, 1 HCOO
13	CH_3O	25	1.1450	1.088	Dimethyl ether :	1 CH_3, 1 CH_3CO
"CH_2O"	CH_2O	26	0.9183	0.780	Diethyl ether :	2 CH_3, 1 CH_2, 1 CH_2O
	CHO	27	0.6908	0.468	Diisopropyl ether :	4 CH_3, 1 CH, 1 CHO
	THF	28	0.9183	1.100	Tetrahydrofuran :	3 CH_2, 1 THF
14	CH_3NH_2	29	1.5959	1.544	Methylamine :	1 CH_3NH_2
"CNH_2"	CH_2NH_2	30	1.3692	1.236	Ethylamine :	1 CH_3, 1 CH_2NH_2
	$CHNH_2$	31	1.1417	0.924	Isopropylamine :	2 CH_3, 1 $CHNH_2$
15	CH_3NH	32	1.4337	1.244	Dimethylamine :	1 CH_3, 1 CH_3NH
"CNH"	CH_2NH	33	1.2070	0.936	Diethylamine :	2 CH_3, 1 CH_2, 1 CH_2NH
	CHNH	34	0.9795	0.624	Diisopropylamine :	4 CH_2, 1 CH, 1 CHNH
16	CH_3N	35	1.1865	0.940	Trimethylamine :	2 CH_3, 1 CH_3N
"(C)3N"	CH_2N	36	0.9597	0.632	Triethylamine :	3 CH_3, 2 CH_2, 1 CH_2N

Table M-1 (continued)

UNIFAC (original-VLE) Group Volume (Rk) and Surface Area (Qk) parameters

Main Group	Sub group	No.	R_k	Q_k	Sample Group Assignment	
17 "$ACNH_2$"	$ACNH_2$	37	1.0600	0.816	Aniline :	5 ACH, 1 $ACNH_2$
18	C_5H_5N	38	2.9993	2.113	Pyridine :	1 C_5H_5N
"Pyridine"	C_5H_4N	39	2.8332	1.833	2-Methylpyridine :	1 CH_3, 1 C_5H_4N
	C_5H_3N	40	2.6670	1.553	2,3-Dimethylpyridine :	2 CH_3, 1 C_5H_3N
19	CH_3CN	41	1.8701	1.724	Acetonitrile :	1 CH_3CN
"CCN"	CH_2CN	42	1.6434	1.416	Propionitrile :	1 CH_3, 1 CH_2CN
20	COOH	43	1.3013	1.224	Acetic acid :	1 CH_3, 1 COOH
"COOH"	HCOOH	44	1.5280	1.532	Formic acid :	1 HCOOH
21	CH_2Cl	45	1.4654	1.264	Butane-1-chloro :	1 CH_3, 2 CH_2,1 CH_2Cl
"CCl"	CHCl	46	1.2380	0.952	Propane-2-chloro :	2 CH_3, 1 CHCl
	CCl	47	1.0106	0.724	2-Methylpropane-2-chloro :	3 CH_3, 1 CCl
22	CH_2Cl_2	48	2.2564	1.998	Methane-dichloro :	1 CH_2Cl_2
"CCl_2"	$CHCl_2$	49	2.0606	1.684	Ethane-1,1-dichloro :	1 CH_3, 1 $CHCl_2$
	CCl_2	50	1.8016	1.448	Propane-2,2-dichloro :	2 CH_3, 1 CCl_2
23	$CHCl_3$	51	2.8700	2.410	Chloroform :	1 $CHCl_3$
"CCl_3"	CCl_3	52	2.6401	2.184	Ethane-1,1,1-trichloro :	1 CH_3, 1 CCl_3
24 "CCl_4"	CCl_4	53	3.3900	2.910	Methane-tetrachloro :	1 CCl_4

Table M-1 (continued)

UNIFAC (original-VLE) Group Volume (Rk) and Surface Area (Qk) parameters

Main Group	Sub group	No.	R_k	Q_k	Sample Group Assignment	
25 "ACCl"	ACCl	54	1.1562	0.844	Benzene-chloro :	5 ACH, 1 ACCl
26 "CNO$_2$"	CH_3NO_2	55	2.0086	1.868	Nitromethane :	1 CH_3NO_2
	CH_2NO_2	56	1.7818	1.560	Propane-1-nitro :	1 CH_3, 1 CH_2, 1 CH_2NO_2
	$CHNO_2$	57	1.5544	1.248	Propane-2-nitro :	2 CH_3, 1 $CHNO_2$
27 "ACNO$_2$"	$ACNO_2$	58	1.4199	1.104	Benzene-nitro :	5 ACH, 1 $ACNO_2$
28 "CS$_2$"	CS_2	59	2.0570	1.650	Carbon disulfide :	1 CS_2
29 "CH$_3$SH"	CH_3SH	60	1.8770	1.676	Methanethiol :	1 CH_3SH
	CH_2SH	61	1.6510	1.368	Ethanethiol :	1 CH_3, 1 CH_2SH
30 "Furfural"	Furfural	62	3.1680	2.484	Furfural :	1 furfural
31 "DOH"	DOH	63	2.4088	2.248	1,2-Ethanediol :	1 DOH
32 "I"	I	64	1.2640	0.992	Iodoethane :	1 CH_3, 1 CH_2, 1 I
33 "Br"	Br	65	0.9492	0.832	Bromoethane :	1 CH_3, 1 CH_2, 1 Br
34 "C$\equiv$C"	$CH\equiv C$	66	1.2920	1.088	Hexyne-1 :	1 CH_3, 3 CH_2, 1 $CH\equiv C$
	$C\equiv C$	67	1.0613	0.784	Hexyne-2 :	2 CH_3, 2 CH_2, 1 $C\equiv C$

Table M-1 (continued)

UNIFAC (original-VLE) Group Volume (Rk) and Surface Area (Qk) parameters

Main Group	Sub Group	No.	R_k	Q_k	Sample Group Assignment	
35 "DMSO"	DMSO	68	2.8266	2.472	Dimethylsulfoxide :	1 DMSO
36 "ACRY"	Acrylnitril	69	2.3144	2.052	Acrylnitrile :	1 Acrylnitril
37 "ClCC"	Cl-(C=C)	70	0.7910	0.724	Ethene-trichloro :	1 CH=C, 3 Cl-(C=C)
38 "ACF"	ACF	71	0.6948	0.524	Hexafluorobenzene :	6 ACF
39	DMF	72	3.0856	2.736	N,N-Dimethylformamide :	1 DMF
"DMF"	$HCON(CH_2)_2$	73	2.6322	2.120	N,N-Diethylformamide :	2 CH_3, 1 $HCON(CH_2)_2$
40	CF_3	74	1.4060	1.380	Perfluorohexane :	2 CF_3, 4 CF_2
"CF_2"	CF_2	75	1.0105	0.920		
	CF	76	0.6150	0.460	Perfluoromethylcyclohexane :	1 CF_3, 5 CF_2, 1 CF
41 "COO"	COO	77	1.3800	1.200	Methyl acrylate :	1 CH_3, 1 CH_2=CH, 1 COO
42	SiH_3	78	1.6035	1.263	Methylsilane :	1 CH_3, 1 SiH_3
"SiH_2"	SiH_2	79	1.4443	1.006	Diethylsilane :	2 CH_3, 2 CH_2, 1 SiH_2
	SiH	80	1.2853	0.749	Heptamethyltrisiloxane :	7 CH_3, 2 SiO, 1 SiH
	Si	81	1.0470	0.410	Heptamethyldisiloxane :	6 CH_3, 1 SiO, 1 Si
43	SiH_2O	82	1.4838	1.062	1,3-Dimethyldisiloxane :	3 CH_3, 1 SiH_2O, 1 SiH
"SiO"	SiHO	83	1.3030	0.764	1,1,3,3-Tetramethyldisiloxane :	4 CH_3, 1 SiHO, 1 SiH
	SiO	84	1.1044	0.466	Octamethylcyclotetrasiloxane :	8 CH_3, 4 SiO

Table M-1 (continued)

UNIFAC (original-VLE) Group Volume (Rk) and Surface Area (Qk) parameters

Main Group	Sub Group	No.	R_k	Q_k	Sample Group Assignment	
44 "NMP"	NMP	85	3.9810	3.200	N-Methylpyrrolidone :	1 NMP
45	CCl_3F	86	3.0356	2.644	Trichlorofluoromethane:	1 CCl_3F
"CClF"	CCl_2F	87	2.2287	1.916	Tetrachloro-1,2-difluoroethane:	2 CCl_2F
	$HCCl_2F$	88	2.4060	2.116	Dichlorofluoromethane:	1 $HCCl_2F$
	HCClF	89	1.6493	1.416	1-Chloro-1,2,2,2-tetrafluoroethane:	1 CF_3, 1 HCClF
	$CClF_2$	90	1.8174	1.648	1,2-Dichlorotetrafluoroethane:	2 $CClF_2$
	$HCClF_2$	91	1.9670	1.828	Chlorodifluoromethane:	1 $HCClF_2$
	$CClF_3$	92	2.1721	2.100	Chlorotrifluoromethane:	1 $CClF_3$
	CCl_2F_2	93	2.6243	2.376	Dichlorodifluoromethane:	1 CCl_2F_2
46	$CONH_2$	94	1.4515	1.248	Acetamid:	1 CH_3, 1 $CONH_2$
"CON"	$CONHCH_3$	95	2.1905	1.796	N-Methylacetamid:	1 CH_3, 1 $CONHCH_3$
	$CONHCH_2$	96	1.9637	1.488	N-Ethylacetamid:	2 CH_3, 1 $CONHCH_2$
	$CON(CH_3)_2$	97	2.8589	2.428	N,N-Dimethylacetamid:	1 CH_3, 1 $CON(CH_3)_2$
	$CONCH_3CH_2$	98	2.6322	2.120	N,N-Methylethylacetamid:	2 CH_3, 1 $CONCH_3CH_2$
	$CON(CH_2)_2$	99	2.4054	1.812	N,N-Diethylacetamid:	3 CH_3, 1 $CON(CH_2)_2$
47	$C_2H_5O_2$	100	2.1226	1.904	2-Ethoxyethanol:	1 CH_3, 1 CH_2, 1 $C_2H_5O_2$
"OCCOH"	$C_2H_4O_2$	101	1.8952	1.592	2-Ethoxy-1-propanol:	2 CH_3, 1 CH_2, 1 $C_2H_4O_2$
48	CH_3S	102	1.6130	1.368	Dimethylsulfide:	1 CH_3, 1 CH_3S
"CH_2S"	CH_2S	103	1.3863	1.060	Diethylsulfide:	2 CH_3, 1 CH_2, 1 CH_2S
	CHS	104	1.1589	0.748	Diisopropylsulfide:	4 CH_3, 1 CH, 1 CHS

Table M-1 (continued)

UNIFAC (original-VLE) Group Volume (Rk) and Surface Area (Qk) parameters						
Main Group	Sub Group	No.	R_k	Q_k	Sample Group Assignment	
49 "morpholine"	MORPH	105	3.4740	2.796	Morpholine:	1 MORPH
50 "thiophene"	C_4H_4S	106	2.8569	2.140	Thiophene:	1 C_4H_4S
	C_4H_3S	107	2.6908	1.860	2-Methylthiophene:	1 CH_3, 1 C_4H_3S
	C_4H_2S	108	2.5247	1.580	2,3-Dimethylthiophene:	2 CH_3, 1 C_4H_2S

Table M-2 : UNIFAC Group-Interaction Parameters for Prediction of Vapor-Liquid-Equilibria at Temperatures Between 250 and 425 K

* Revised UNIFAC Group-Interaction Parameters

o UNIFAC Parameters for Group-Interactions Previously not Available (n.a.)

\# UNIFAC Group-Interaction Parameters for New Groups

	1 CH_2	2 C=C	3 ACH	4 $ACCH_2$	5 OH	6 CH_3OH
1 CH_2	0.0	86.02	61.13	76.50	986.5	697.2
2 C=C	-35.36	0.0	38.81	74.15	524.1	787.6
3 ACH	-11.12	3.446	0.0	167.0	636.1	637.4
4 $ACCH_2$	-69.70	-113.6	-146.8	0.0	803.2	603.3
5 OH	156.4	457.0	89.60	25.82	0.0	-137.1
6 CH_3OH	16.51	-12.52	-50.00	-44.50	249.1	0.0
7 H_2O	300.0	496.1	362.3	377.6	-229.1	289.6
8 ACOH	275.8	217.5	25.34	244.2	-451.6	-265.2
9 CH_2CO	26.76	42.92	140.1	365.8	164.5	108.7
10 CHO	505.7	56.30	23.39	106.0	529.0^{*}	-340.2
11 CCOO	114.8	132.1	85.84	-170.0	245.4	249.6
12 HCOO	329.3^{*}	110.4^{*}	18.12^{*}	428.0^{*}	139.4^{*}	227.8^{*}
13 CH_2O	83.36	26.51	52.13	65.69	237.7	238.4
14 CNH_2	-30.48	1.163	-44.85	296.4^{o}	-242.8^{*}	-481.7
15 CNH	65.33	-28.70	-22.31	223.0	-150.0	-370.3^{*}
16 $(C)_3N$	-83.98	-25.38	-223.9	109.9	28.60	-406.8
17 $ACNH_2$	1139.	2000.	247.5	762.8	-17.40	-118.1
18 Pyridine	-101.6	-47.63^{o}	31.87	49.80	-132.3	-378.2
19 CCN	24.82	-40.62	-22.97	-138.4	185.4	162.6^{*}
20 COCH	315.3	1264.	62.32	89.86^{*}	-151.0	339.8^{*}
21 CCl	91.46	40.25^{*}	4.680	122.9	562.2	529.0
22 CCl_2	34.01	-23.50^{*}	121.3	140.8	527.6^{*}	669.9
23 CCl_3	36.70	51.06	288.5	69.90^{*}	742.1	649.1
24 CCl_4	-78.45	160.9	-4.700	134.7	856.3	709.6^{*}
25 ACCl	106.8^{*}	70.32^{*}	-97.27^{*}	402.5^{*}	325.7^{*}	612.8^{*}
26 CNO_2	-32.69	-1.996	10.38	-97.05	261.6	252.6
27 $ACNO_2$	5541.	n.a.	1824.	-127.8	561.6	n.a.
28 CS_2	-52.65	16.62	21.50	40.68	609.8^{*}	914.2
29 CH_3SH	-7.481	n.a.	28.41	19.56^{o}	461.6	448.6^{*}
30 Furfural	-25.31	82.64^{o}	157.3	128.8^{*}	521.6	n.a.
31 DOH	139.9	n.a.	221.4	150.6	267.6	240.8^{o}
32 I	128.0	n.a.	58.68	26.41^{o}	501.3	431.3^{o}
33 Br	-31.52	174.6^{o}	-154.2^{*}	$1112.^{*}$	524.9	494.7
34 C≡C	-72.88	41.38	n.a.	n.a.	68.95^{o}	n.a.
35 DMSO	50.49	64.07^{*}	-2.504	-143.2	-25.87	695.0
36 ACRY	-165.9	573.0^{o}	-123.6^{o}	397.4^{o}	389.3^{o}	218.8^{o}
37 ClCC	47.41	124.2	395.8	419.1^{o}	738.9	528.0
38 ACF	-5.132	-131.7^{o}	-237.2	-157.3	649.7	645.9
39 DMF	-31.95	249.0	-133.9	-240.2	64.16	172.2
40 CF_2	147.3	62.40^{o}	140.6^{o}	n.a.	n.a.	n.a.
41 COO	529.0	1397.	317.6	615.8	88.63	171.0
42 SiH_2	-34.36	n.a.	787.9	n.a.	1913.	n.a.
43 SiO	110.2	n.a.	234.4	n.a.	n.a.	n.a.
44 NMP	13.89	-16.11^{o}	-23.88	6.214	796.9	n.a.
45 CClF	$30.74^{\#}$	n.a.	$167.9^{\#}$	n.a.	$794.4^{\#}$	$762.7^{\#}$
46 CON	$27.97^{\#}$	$9.755^{\#}$	n.a.	n.a.	$394.8^{\#}$	n.a.
47 OCCOH	$-11.92^{\#}$	$132.4^{\#}$	$-86.88^{\#}$	$-19.45^{\#}$	$517.5^{\#}$	n.a.
48 CH_2S	$39.93^{\#}$	$543.6^{\#}$	n.a.	n.a.	n.a.	$420.0^{\#}$
49 Morph	$-23.61^{\#}$	$161.1^{\#}$	$142.9^{\#}$	$274.1^{\#}$	$-61.20^{\#}$	$-89.24^{\#}$
50 Thiophene	$-8.479^{\#}$	n.a.	$23.93^{\#}$	$2.845^{\#}$	$682.5^{\#}$	$597.8^{\#}$

	7 H_2O	8 ACOH	9 CH_2CO	10 CHO	11 CCOO	12 HCOO
1 CH_2	1318.	1333.	476.4	677.0	232.1	507.0*
2 C=C	270.6	526.1	182.6	448.8	37.85	333.5*
3 ACH	903.8	1329.	25.77	347.3	5.994	287.1*
4 $ACCH_2$	5695.	884.9	-52.10	586.8	5688.	197.8*
5 OH	353.5	-259.7	84.00	-203.6*	101.1	267.8*
6 CH_3OH	-181.0	-101.7	23.39	306.4	-10.72	179.7*
7 H_2O	0.0	324.5	-195.4	-116.0*	72.87	n.a.
8 ACOH	-601.8	0.0	-356.1	-271.1°	-449.4	n.a.
9 CH_2CO	472.5	-133.1	0.0	-37.36	-213.7	-190.4*
10 CHO	480.8*	-155.6°	128.0	0.0	-110.3	766.0*
11 CCOO	200.8	-36.72	372.2	185.1	0.0	-241.8*
12 HCOO	n.a.	n.a.	385.4*	-236.5*	1167.*	0.0
13 CH_2O	-314.7	-178.5°	191.1	-7.838	461.3	457.3°
14 CNH_2	-330.4	n.a.	n.a.	n.a.	n.a.	n.a.
15 CNH	-448.2	n.a.	394.6°	n.a.	136.0	n.a.
16 $(C)_3N$	-598.8	n.a.	225.3	n.a.	2889.$^\circ$	n.a.
17 $ACNH_2$	-341.6*	-253.1	-450.3	n.a.	-294.8	n.a.
18 Pyridine	-332.9	-341.6	29.10*	n.a.	n.a.	554.4°
19 CCN	242.8	n.a.	-287.5	n.a.	-266.6	99.37°
20 COOH	-66.17	-11.00°	-297.8	-165.5°	-256.3	193.9*
21 CCl	698.2	n.a.	286.3	-47.51	35.38	n.a.
22 CCl_2	708.7	n.a.	82.86*	190.6°	-133.0	n.a.
23 CCl_3	826.8	n.a.	552.1	242.8	176.5	235.6*
24 CCl_4	1201.	10000.	372.0	n.a.	129.5	351.9*
25 ACCl	-274.5*	622.3°	518.4*	n.a.	-171.1*	383.3°
26 CNO_2	417.9	n.a.	-142.6	n.a.	129.3	n.a.
27 $ACNO_2$	360.7	n.a.	-101.5°	n.a.	n.a.	n.a.
28 CS_2	1081.	1421.$^\circ$	303.7	n.a.	243.8	n.a.
29 CH_3SH	n.a.	n.a.	160.6	n.a.	n.a.	201.5*
30 Furfural	23.48	n.a.	317.5*	n.a.	-146.3	n.a.
31 DOH	-137.4*	838.4	135.4°	n.a.	152.0	n.a.
32 I	n.a.	n.a.	138.0	245.9°	21.92	n.a.
33 Br	n.a.	n.a.	-142.6	n.a.	24.37	n.a.
34 $C\equiv C$	n.a.	n.a.	443.6	n.a.	n.a.	n.a.
35 DMSO	-240.0	n.a.	110.4	n.a.	41.57	n.a.
36 ACRY	386.6	n.a.	n.a.	354.0°	175.5	n.a.
37 ClCC	n.a.	n.a.	-40.90	183.8°	611.3*	134.5°
38 ACF	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
39 DMF	-287.1	n.a.	97.04	13.89°	-82.12°	-116.7°
40 CF_2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
41 COO	284.4	-167.3	123.4	577.5°	-234.9	145.4*
42 SiH_2	180.2°	n.a.	992.4	n.a.	n.a.	n.a.
43 SiO	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
44 NMP	832.2	-234.7°	n.a.	n.a.	n.a.	n.a.
45 CClF	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
46 CON	-509.3‡	n.a.	n.a.	n.a.	n.a.	n.a.
47 OCCOH	-205.7‡	n.a.	156.4‡	n.a.	-3.444‡	n.a.
48 CH_2S	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
49 Morph	-384.3‡	n.a.	n.a.	n.a.	n.a.	n.a.
50 Thiophene	n.a.	810.5‡	278.8‡	n.a.	n.a.	n.a.

	13 CH_2O	14 CNH_2	15 CNH	16 $(C)_3N$	17 $ACNH_2$	18 Pyridine
1 CH_2	251.5	391.5	255.7	206.6	920.7	287.8
2 C=C	214.5	240.9	163.9	61.11	749.3	280.5°
3 ACH	32.14	161.7	122.8	90.49	648.2	-4.449
4 $ACCH_2$	213.1	19.02°	-49.29	23.50	664.2	52.80
5 OH	28.06	8.642*	42.70	-323.0	-52.39	170.0
6 CH_3OH	-128.6	359.3	-20.98*	53.90	489.7	580.5
7 H_2O	540.5	48.89	168.0	304.0	243.2*	459.0
8 ACOH	-162.9°	n.a.	n.a.	n.a.	119.9	-305.5
9 CH_2CO	-103.6	n.a.	-174.2°	-169.0	6201.	7.341*
10 CHO	304.1	n.a.	n.a.	n.a.	n.a.	n.a.
11 CCOO	-235.7	n.a.	-73.50	-196.7°	475.5	n.a.
12 HCOO	-234.0°	n.a.	n.a.	n.a.	n.a.	-233.4°
13 CH_2O	0.0	-78.36°	251.5*	5422.$^{\circ}$	n.a.	213.2°
14 CNH_2	222.1°	0.0	-107.2*	-41.11	-200.7	n.a.
15 CNH	-56.08*	127.4*	0.0	-189.2	n.a.	n.a.
16 $(C)_3N$	-194.1°	38.89	865.9	0.0	n.a.	n.a.
17 $ACNH_2$	n.a.	-15.07	n.a.	n.a.	0.0	89.70°
18 Pyridine	-156.1°	n.a.	n.a.	n.a.	117.4°	0.0
19 CCN	38.81	-157.3°	-108.5°	n.a.	777.4	134.3
20 COOH	-338.5	n.a.	n.a.	n.a.	493.8°	-313.5
21 CCl	225.4	131.2°	n.a.	n.a.	429.7	n.a.
22 CCl_2	-197.7	n.a.	n.a.	-141.4	140.8	587.3
23 CCl_3	-20.93	n.a.	n.a.	-293.7	n.a.	18.98
24 CCl_4	113.9	261.1	91.13	316.9*	898.2	368.5*
25 ACCl	-25.15*	108.5*	102.2*	2951.*	334.9*	n.a.
26 CNO_2	-94.49	n.a.	n.a.	n.a.	n.a.	n.a.
27 $ACNO_2$	n.a.	n.a.	n.a.	n.a.	134.9	2475.$^{\circ}$
28 CS_2	112.4	n.a.	n.a.	n.a.	n.a.	n.a.
29 CH_3SH	63.71	106.7	n.a.	n.a.	n.a.	n.a.
30 Furfural	-87.31°	n.a.	n.a.	n.a.	n.a.	n.a.
31 DCH	9.207	n.a.	n.a.	n.a.	192.3*	n.a.
32 I	476.6	n.a.	n.a.	n.a.	n.a.	n.a.
33 Br	736.4	n.a.	n.a.	n.a.	n.a.	-42.71°
34 C=C	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
35 DMSO	-93.51*	n.a.	n.a.	-257.2	n.a.	n.a.
36 ACRY	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
37 ClCC	-217.9	n.a.	n.a.	n.a.	n.a.	281.6°
38 ACF	167.3	n.a.	-198.8°	116.5	n.a.	159.8°
39 DMF	-158.2	49.70°	n.a.	-185.2°	343.7	n.a.
40 CF_2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
41 COO	-247.8	n.a.	284.5	n.a.	-22.10	n.a.
42 SiH_2	448.5°	961.8°	1464.$^{\circ}$	n.a.	n.a.	n.a.
43 SiO	n.a.	-125.2°	1604.$^{\circ}$	n.a.	n.a.	n.a.
44 NMP	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
45 CClF	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
46 CON	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
47 OCCOH	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
48 CH_2S	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
49 Morph	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
50 Thiophene	n.a.	n.a.	n.a.	n.a.	n.a.	221.4$^{\#}$

	19 CCN	20 COOH	21 CCl	22 CCl_2	23 CCl_3	24 CCl_4
1 CH_2	597.0	663.5	35.93	53.76	24.90	104.3
2 C=C	336.9	318.9	-36.87*	58.55*	-13.99	-109.7
3 ACH	212.5	537.4	-18.81	-144.4	-231.9	3.000
4 $ACCH_2$	6096.	872.3*	-114.1	-111.0	-80.25*	-141.3
5 OH	6.712	199.0	75.62	65.28*	-98.12	143.1
6 CH_3OH	53.28*	-202.0*	-38.32	-102.5	-139.4	-44.76*
7 H_2O	112.6	-14.09	325.4	370.4	353.7	497.5
8 ACOH	n.a.	408.9°	n.a.	n.a.	n.a.	1827.
9 CH_2CO	481.7	669.4	-191.7	-130.3*	-354.6	-39.20
10 CHO	n.a.	497.5°	751.9	67.52°	-483.7	n.a.
11 CCOO	494.6	660.2	-34.74	108.9	-209.7	54.57
12 HCOO	-47.25°	-268.1*	n.a.	n.a.	-126.2*	179.7*
13 CH_2O	-18.51	664.6	301.1	137.8	-154.3	47.67
14 CNH_2	358.9°	n.a.	-82.92°	n.a.	n.a.	-99.81
15 CNH	147.1°	n.a.	n.a.	n.a.	n.a.	71.23
16 $(C)_3N$	n.a.	n.a.	n.a.	-73.85	-352.9	-262.0*
17 $ACNH_2$	-281.6	-396.0°	287.0	-111.0	n.a.	882.0
18 Pyridine	-169.7	-153.7	n.a.	-351.6	-114.7	-205.3*
19 CCN	0.0	n.a.	4.933*	-152.7	-15.62	-54.86
20 COOH	n.a.	0.0	13.41*	-44.70*	39.63*	183.4*
21 CCl	54.32*	519.1*	0.0	108.3	249.6	62.42
22 CCl_2	258.6	543.3*	-84.53	0.0	0.0000	56.33
23 CCl_3	74.04	504.2*	-157.1	0.0000	0.0	-30.10
24 CCl_4	492.0	631.0*	11.80	17.97	51.90	0.0
25 ACCl	363.5*	993.4°	-129.7*	-8.309°	-0.2266°	248.4*
26 CNO_2	0.2830	n.a.	113.0	-9.639°	n.a.	-34.68
27 $ACNO_2$	n.a.	n.a.	1971.°	n.a.	n.a.	514.6
28 CS_2	335.7	n.a.	-73.09	n.a.	-26.06	-60.71
29 CH_3SH	161.0*	n.a.	-27.94	n.a.	n.a.	n.a.
30 Furfural	n.a.	570.6°	n.a.	n.a.	48.48	-133.2
31 DOH	169.6°	n.a.	n.a.	n.a.	n.a.	n.a.
32 I	n.a.	616.6°	n.a.	-40.82	21.76	48.49
33 Br	136.9°	5256.	-262.3*	-174.5°	n.a.	77.55*
34 C=C	329.1	n.a.	n.a.	n.a.	n.a.	n.a.
35 DMSO	n.a.	-180.2°	n.a.	-215.0	-343.6	-58.43
36 ACRY	-42.31	n.a.	n.a.	n.a.	n.a.	-85.15
37 ClCC	335.2*	898.2	383.2*	301.9°	-149.8	-134.2
38 ACF	n.a.	n.a.	n.a.	n.a.	n.a.	-124.6
39 DMF	150.6°	-97.77°	n.a.	n.a.	n.a.	-186.7
40 CF_2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
41 COO	-61.6	1179.	182.2	305.4	-193.0	335.7
42 SiH_2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
43 SiO	n.a.	n.a.	n.a.	n.a.	n.a.	70.81
44 NMP	n.a.	n.a.	n.a.	n.a.	-196.2°	n.a.
45 CClF	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
46 CON	n.a.	-70.25‡	n.a.	n.a.	n.a.	n.a.
47 OCCOH	119.2‡	n.a.	n.a.	-194.7‡	n.a.	3.163‡
48 CH_2S	n.a.	n.a.	n.a.	n.a.	-363.1‡	-11.30‡
49 Morph	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
50 Thiophene	n.a.	n.a.	n.a.	n.a.	n.a.	-79.34‡

	31 DOH	32 I	33 Br	34 C=C	35 DMSO	36 ACRY
1 CH_2	3025.	335.8	479.5	298.9	526.5	689.0
2 C=C	n.a.	n.a.	183.8°	31.14	179.0*	-52.87°
3 ACH	210.7	113.3	261.3*	n.a.	169.9	383.9°
4 $ACCH_2$	4975.	259.0°	210.0*	n.a.	4284.	-119.2°
5 CH	-318.9	313.5	202.1	727.8°	-202.1	74.27°
6 CH_3OH	-119.2°	212.1°	106.3	n.a.	-399.3	-5.224°
7 H_2O	12.72*	n.a.	n.a.	n.a.	-139.0	160.8
8 ACOH	-687.1	n.a.	n.a.	n.a.	n.a.	n.a.
9 CH_2CO	71.46°	53.59	245.2	-246.6	-44.58	n.a.
10 CHO	n.a.	117.0°	n.a.	n.a.	n.a.	-339.2°
11 CCOO	-101.7	148.3	18.88	n.a.	52.08	-28.61
12 HCOO	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
13 CH_2O	-20.11	-149.5	-202.3	n.a.	128.8*	n.a.
14 CNH_2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
15 CNH	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
16 $(C)_3N$	n.a.	n.a.	n.a.	n.a.	243.1	n.a.
17 $ACNH_2$	0.1004*	n.a.	n.a.	n.a.	n.a.	n.a.
18 Pyridine	n.a.	n.a.	-60.78°	n.a.	n.a.	n.a.
19 CCN	177.5°	n.a.	-62.17°	-203.0	n.a.	81.57
20 COOH	n.a.	228.4°	-95.00	n.a.	-463.6°	n.a.
21 CCl	n.a.	n.a.	344.4*	n.a.	n.a.	n.a.
22 CCl_2	n.a.	177.6	315.9°	n.a.	215.0	n.a.
23 CCl_3	n.a.	86.40	n.a.	n.a.	363.7	n.a.
24 CCl_4	n.a.	247.8	146.6*	n.a.	337.7	369.5
25 ACCl	n.a.	n.a.	593.4*	n.a.	n.a.	n.a.
26 CNO_2	139.8	304.3	10.17	-27.70	n.a.	n.a.
27 $ACNO_2$	n.a.	2990.$^{\circ}$	-124.0°	n.a.	n.a.	n.a.
28 CS_2	n.a.	292.7°	n.a.	n.a.	n.a.	n.a.
29 CH_3SH	n.a.	n.a.	n.a.	n.a.	31.66	n.a.
30 Furfural	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
31 DOH	0.0	n.a.	n.a.	n.a.	-417.2	n.a.
32 I	n.a.	0.0	n.a.	n.a.	n.a.	n.a.
33 Br	n.a.	n.a.	0.0	n.a.	32.90°	n.a.
34 C=C	n.a.	n.a.	n.a.	0.0	n.a.	n.a.
35 DMSO	535.8	n.a.	-111.2°	n.a.	0.0	n.a.
36 ACRY	n.a.	n.a.	n.a.	n.a.	n.a.	0.0
37 ClCC	n.a.	n.a.	n.a.	631.5°	n.a.	837.2°
38 ACF	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
39 DMF	-191.7	n.a.	n.a.	6.699	136.6	5.150°
40 CF_2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
41 COO	-264.3°	288.1	627.7°	n.a.	-29.34	-53.91
42 SiH_2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
43 SiO	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
44 NMP	262.0°	n.a.	n.a.	n.a.	n.a.	n.a.
45 CClF	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
46 CON	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
47 OCCOH	515.8‡	n.a.	n.a.	n.a.	n.a.	n.a.
48 CH_2S	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
49 Morph	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
50 Thiophene	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

Table III-2 (Concluded)

	37 ClCC	38 ACF	39 DMF	40 CF_2	41 COO	42 SiH_2
1 CH_2	-4.189	125.8	485.3	-2.859	387.1	-450.4
2 C=C	-66.46	359.3^{o}	-70.45	449.4^{o}	48.33	n.a.
3 ACH	-259.1	389.3	245.6	22.67^{o}	103.5	-432.3
4 $ACCH_2$	-282.5^{o}	101.4	5629.	n.a.	69.26	n.a.
5 OH	225.8	44.78	-143.9	n.a.	190.3	-817.7
6 CH_3OH	33.47	-48.25	-172.4	n.a.	165.7	n.a.
7 H_2O	n.a.	n.a.	319.0	n.a.	-197.5	-363.8^{o}
8 ACOH	n.a.	n.a.	n.a.	n.a.	-494.2	n.a.
9 CH_2CO	-34.57	n.a.	-61.70	n.a.	-18.80	-588.9
10 CHO	172.4^{o}	n.a.	-268.8^{o}	n.a.	-275.5^{o}	n.a.
11 CCOO	-275.2*	n.a.	85.33^{o}	n.a.	560.2	n.a.
12 HCOO	-11.40^{o}	n.a.	308.9^{o}	n.a.	-122.3*	n.a.
13 CH_2O	240.2	-274.0	254.8	n.a.	417.0	1338.^{o}
14 CNH_2	n.a.	n.a.	-164.0^{o}	n.a.	n.a.	-664.4^{o}
15 CNH	n.a.	570.9^{o}	n.a.	n.a.	-38.77	448.1^{o}
16 $(C)_3N$	n.a.	-196.3	22.05^{o}	n.a.	n.a.	n.a.
17 $ACNH_2$	n.a.	n.a.	-334.4	n.a.	-89.42	n.a.
18 Pyridine	160.7^{o}	-158.8^{o}	n.a.	n.a.	n.a.	n.a.
19 CCN	-55.77*	n.a.	-151.5^{o}	n.a.	120.3	n.a.
20 COOH	-11.16	n.a.	-228.0^{o}	n.a.	-337.0	n.a.
21 CCl	-168.2*	n.a.	n.a.	n.a.	63.67	n.a.
22 CCl_2	-91.80^{o}	n.a.	n.a.	n.a.	-96.87	n.a.
23 CCl_3	111.2	n.a.	n.a.	n.a.	255.8	n.a.
24 CCl_4	187.1	215.2	498.6	n.a.	256.5	n.a.
25 ACCl	n.a.	n.a.	n.a.	n.a.	-71.18*	n.a.
26 CNO_2	10.76	n.a.	-223.1^{o}	n.a.	248.4	n.a.
27 $ACNO_2$	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
28 CS_2	-47.37	n.a.	n.a.	n.a.	469.8	n.a.
29 CH_3SH	n.a.	n.a.	78.92	n.a.	n.a.	n.a.
30 Furfural	n.a.	n.a.	n.a.	n.a.	43.37^{o}	n.a.
31 DOH	n.a.	n.a.	302.2	n.a.	347.8^{o}	n.a.
32 I	n.a.	n.a.	n.a.	n.a.	68.55	n.a.
33 Br	n.a.	n.a.	n.a.	n.a.	-195.1^{o}	n.a.
34 C≡C	2073.^{o}	n.a.	-119.8	n.a.	n.a.	n.a.
35 DMSO	n.a.	n.a.	-97.71	n.a.	153.7	n.a.
36 ACRY	-208.8^{o}	n.a.	-8.804^{o}	n.a.	423.4	n.a.
37 ClCC	0.0	n.a.	255.0^{o}	n.a.	730.8	n.a.
38 ACF	n.a.	0.0	n.a.	-117.2	n.a.	n.a.
39 DMF	-137.7^{o}	n.a.	0.0	-5.579^{o}	72.31^{o}	n.a.
40 CF_2	n.a.	185.6	55.80^{o}	0.0	n.a.	n.a.
41 COO	-198.0	n.a.	-28.65^{o}	n.a.	0.0	n.a.
42 SiH_2	n.a.	n.a.	n.a.	n.a.	n.a.	0.0
43 SiO	n.a.	n.a.	n.a.	n.a.	n.a.	745.3
44 NMP	-66.31^{o}	n.a.	n.a.	n.a.	n.a.	n.a.
45 CClF	n.a.	n.a.	n.a.	-32.17‡	n.a.	n.a.
46 CON	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
47 OCCOH	n.a.	n.a.	n.a.	n.a.	101.2‡	n.a.
48 CH_2S	148.9‡	n.a.	n.a.	n.a.	n.a.	n.a.
49 Morph	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
50 Thiophene	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

Table M-2 (Continued)

	43 SiO	44 NMP	45 ClF	46 CON	47 OCCOH	48 CH_2S
1 CH_2	252.7	220.3	-5.869[#]	390.9[#]	553.3[#]	187.0[#]
2 C=C	n.a.	86.46°	n.a.	200.2[#]	268.1[#]	-617.0[#]
3 ACH	238.9	30.04	-88.11[#]	n.a.	333.3[#]	n.a.
4 $ACCH_2$	n.a.	46.38	n.a.	n.a.	421.9[#]	n.a.
5 OH	n.a.	-504.2	72.96[#]	-382.7[#]	-248.3[#]	n.a.
6 CH_3CH	n.a.	n.a.	-52.10[#]	n.a.	n.a.	37.63[#]
7 H_2O	n.a.	-452.2	n.a.	835.6[#]	139.6[#]	n.a.
8 ACCH	n.a.	-659.0°	n.a.	n.a.	n.a.	n.a.
9 CH_2CO	n.a.	n.a.	n.a.	n.a.	37.54[#]	n.a.
10 CHO	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
11 CCOO	n.a.	n.a.	n.a.	n.a.	151.8[#]	n.a.
12 HCOO	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
13 CH_2O	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
14 CNH_2	275.9°	n.a.	n.a.	n.a.	n.a.	n.a.
15 CNH	-1327.°	n.a.	n.a.	n.a.	n.a.	n.a.
16 $(C)_3N$	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
17 $ACNH_2$	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
18 Pyridine	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
19 CCN	n.a.	n.a.	n.a.	n.a.	16.23[#]	n.a.
20 COOH	n.a.	n.a.	n.a.	-322.3[#]	n.a.	n.a.
21 CCl	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
22 CCl_2	n.a.	n.a.	n.a.	n.a.	361.1[#]	n.a.
23 CCl_3	n.a.	-35.68°	n.a.	n.a.	n.a.	565.9[#]
24 CCl_4	233.1	n.a.	n.a.	n.a.	423.1[#]	63.95[#]
25 ACCl	n.a.	-209.7°	n.a.	n.a.	434.1[#]	n.a.
26 CNO_2	n.a.	n.a.	-218.9[#]	n.a.	n.a.	n.a.
27 $ACNO_2$	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
28 CS_2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
29 CH_3SH	n.a.	1004.°	n.a.	n.a.	n.a.	-18.27[#]
30 Furfural	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
31 DOH	n.a.	-262.0°	n.a.	n.a.	-353.5[#]	n.a.
32 I	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
33 Br	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
34 C≡C	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
35 DMSO	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
36 ACRY	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
37 ClCC	n.a.	26.35°	n.a.	n.a.	n.a.	2429.[#]
38 ACF	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
39 DMF	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
40 CF_2	n.a.	n.a.	111.8[#]	n.a.	n.a.	n.a.
41 COO	n.a.	n.a.	n.a.	n.a.	122.4[#]	n.a.
42 SiH_2	-2166.	n.a.	n.a.	n.a.	n.a.	n.a.
43 SiO	0.0	n.a.	n.a.	n.a.	n.a.	n.a.
44 NMP	n.a.	0.0	n.a.	n.a.	n.a.	n.a.
45 CClF	n.a.	n.a.	0.0	n.a.	n.a.	n.a.
46 CON	n.a.	n.a.	n.a.	0.0	n.a.	n.a.
47 OCCOH	n.a.	n.a.	n.a.	n.a.	0.0	n.a.
48 CH_2S	n.a.	n.a.	n.a.	n.a.	n.a.	0.0
49 Morph	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
50 Thiophene	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.

Table M-2 (continued)

	49 Morph	50 Thiophene
1 CH_2	216.1[‡]	92.99[‡]
2 C=C	62.56[‡]	n.a.
3 ACH	-59.58[‡]	-39.16[‡]
4 $ACCH_2$	-203.6[‡]	184.9[‡]
5 OH	104.7[‡]	57.65[‡]
6 CH_3OH	-59.40[‡]	-46.01[‡]
7 H_2O	407.9[‡]	n.a.
8 ACOH	n.a.	1005.[‡]
9 CH_2CO	n.a.	-162.6[‡]
10 CHO	n.a.	n.a.
11 CCOO	n.a.	n.a.
12 HCOO	n.a.	n.a.
13 CH_2O	n.a.	n.a.
14 CNH_2	n.a.	n.a.
15 CNH	n.a.	n.a.
16 $(C)_3N$	n.a.	n.a.
17 $ACNH_2$	n.a.	n.a.
18 Pyridine	n.a.	-136.6[‡]
19 CCN	n.a.	n.a.
20 COOH	n.a.	n.a.
21 CCl	n.a.	n.a.
22 CCl_2	n.a.	n.a.
23 CCl_3	n.a.	n.a.
24 CCl_4	n.a.	108.5[‡]
25 ACCl	n.a.	n.a.
26 CNO_2	n.a.	-4.565[‡]
27 $ACNO_2$	n.a.	n.a.
28 CS_2	n.a.	n.a.
29 CH_3SH	n.a.	n.a.
30 Furfural	n.a.	n.a.
31 DOH	n.a.	n.a.
32 I	n.a.	n.a.
33 Br	n.a.	n.a.
34 C=C	n.a.	n.a.
35 DMSO	n.a.	n.a.
36 ACRY	n.a.	n.a.
37 ClCC	n.a.	n.a.
38 ACF	n.a.	n.a.
39 DMF	n.a.	n.a.
40 CF_2	n.a.	n.a.
41 COO	n.a.	n.a.
42 SiH_2	n.a.	n.a.
43 SiO	n.a.	n.a.
44 NMP	n.a.	n.a.
45 CClF	n.a.	n.a.
46 CON	n.a.	n.a.
47 OCCOH	n.a.	n.a.
48 CH_2S	n.a.	n.a.
49 Morph	0.0	n.a.
50 Thiophene	n.a.	0.0

Table M-3

UNIFAC Group Volume (R_k) and Surface Area (Q_k) Parameters						
Main Group	Sub group	No.	R_k	Q_k	Sample Group Assignment	
1. "CH_2"	CH_3	1	0.9011	0.848	Hexane:	2 CH_3, 4 CH_2
	CH_2	2	0.6744	0.540		
	CH	3	0.4469	0.228	2-Methylpropane:	3 CH_3, 1 CH
	C	4	0.2195	0.000	Neopentane:	4 CH_3, 1 C
2. "C=C"	CH_2=CH	5	1.3454	1.176	Hexene-1:	1 CH_3, 3 CH_2, 1 CH_2=CH
	CH=CH	6	1.1167	0.867	Hexene-2:	2 CH_3, 2 CH_2, 1 CH=CH
	CH_2=C	7	1.1173	0.988	2-Methyl-1-butene:	2 CH_3, 1 CH_2, 1 CH_2=C
	CH=C	8	0.8886	0.676	2-Methyl-2-butene:	2 CH_3, 1 CH=C
	C=C	9	0.6605	0.485	2,3-Dimethylbutene:	4 CH_3, 1 C=C
3. "ACH"	ACH	10	0.5313	0.400	Naphthaline:	8 ACH, 2 AC
	AC	11	0.3652	0.120	Styrene:	1 CH_2=CH, 5 ACH, 1AC
4. "$ACCH_2$"	$ACCH_3$	12	1.2663	0.968	Toluene:	5 ACH, 1 ACH_3
	$ACCH_2$	13	1.0396	0.660	Ethylbenzene:	1 CH_3, 5 ACH, 2 $ACCH_2$
	ACCH	14	0.8121	0.348	Cumene:	2 CH_3, 5 AC, 1 ACCH
5. "OH"	OH	15	1.0000	1.200	Propanol-2:	2 CH_3, 1 CH, 1 OH
6. CH_3OH"	CH_3OH	16	1.4311	1.432	Methanol:	1 CH_3OH
7. "H_2O"	H_2O	17	0.9200	1.400	Water:	1 H_20
8. "ACOH"	ACOH	18	0.8952	0.680	Phenol:	5 ACOH, 1 ACOH
9. "CH_2CO	CH_3CO	19	1.6724	1.448	Butanone:	1 CH_3, 1 CH_2, 1 CH_3CO
	CH_2CO	20	1.4457	1.180	Pentanone-3:	2 CH_3, 1 CH_2, 1 CH_2CO
10. "CHO"	CHO	21	0.9980	0.948	Propionoic aldehyde:	1 CH_3, 1 CH_2, 1 CHO
11. "CCOO"	CH_3COO	22	1.9031	1.728	Butyl acetate:	1 CH_3, 3 CH_2, 1 CH_3COO
	CH_2COO	23	1.6764	1.420	Methyl propionate:	2 CH_3, 1 CH_2COO
12. "HCOO"	HCOO	24	1.2420	1.188	Ethyl formate:	1 CH_3, 1 CH_2,1 HCOO

Table M-3 (Continued)

UNIFAC Group Volume (R_k) and Surface Area (Q_k) Parameters

Main Group	Sub group	No.	R_k	Q_k	Sample Group Assignment	
13. CH_2O"	CH_3O CH_2O CHO THF	25 26 27 28	1.1450 0.9183 0.6908 0.9183	1.088 0.780 0.468 1.100	Dimethyl ether: Diethyl ether: Diisopropyl ether: Tetrahydrofuran:	1 CH_3, 1 CH_3CO 2 CH_3, 1 CH_2, 1 CH_2O 4 CH_3, 1 CH, 1 CHO 3 CH_2, 1 THF
14. "CNH"	CH_3NH CH_2NH CHNH	29 30 31	1.4337 1.2070 0.9795	1.244 0.936 0.624	Dimethylamine: Diethylamine: Diisopropylamine:	1 CH_3, 1 CH_3 2 CH_3, 1 CH_2, 1 CH_2NH 4 CH_2, 1 CH, 1 CHNH
15. "$(C)_3N$"	CH_3N CH_2N	32 33	1.1865 0.9597	0.940 0.632	Trimethylamine: Triethylamine:	2 CH_3, 1 CH_3N 3 CH_3, 2 CH_2, 1 CH_2N
16. "$ACNH_2$"	$ACNH_2$	34	1.0600	0.816	Aniline:	5 ACH, 1 $ACNH_2$
17. "Pyridine"	C_5H_5N C_5H_4N C_5H_3N	35 36 37	2.9993 2.8332 2.6670	2.113 1.833 1.553	Pyridine: 2-Methylpyridine: 2,3-Dimethylpyridine:	1 C_5H_5N 1 CH_3, 1 C_5H_4N 2 CH_3, 1 C_5H_5N
18. "CCN"	CH_3CN CH_2CN	38 39	1.8701 1.6434	1.724 1.416	Acetonitrile: Propinotrille	1 CH_3,CN 1 CH_3, 1 CH_2CN
19. "COOH"	COOH HCOOH	40 41	1.3013 1.5280	1.224 1.532	Acetic acid: Formic acid:	1 CH_3, 1 COOH 1 HCOOH
20. "CCL"	CH_2Cl CHCl CCl	42 43 44	1.4654 1.2380 1.0006	1.264 0.952 0.724	Butane-1-chloro: Propane-2-chloro: 2-Methylpropane-2-chloro:	1 CH_3, 2 CH_2, 1 CH_2Cl 2 CH_3, 1 CHCl 3 CH_3, 1 CCL
21. "CCl_2"	CH_2Cl_2 $CHCl_2$ CCl_2	45 46 47	2.2564 2.0606 1.8016	1.988 1.684 1.448	Methane-dichloro: Ethane-1,1-dichloro: Propane-2,2-dichloro:	1 CH_2Cl_2 1 CH_3, 1 $CHCl_2$ 2 CH_3, 1 CCl_2
22. "CCl_3"	$CHCl_3$ CCl_3	48 49	2.8700 2.6401	2.410 2.184	Chloroform: Ethane-1,1,1-trichloro:	1 $CHCl_3$ 1 CH_3, 1 CCl_3
23. "CCl_4"	CCl_4	50	3.3900	2.910	Methane-tetrachloro:	1 CCl_4

Table M-3 (Continued)

UNIFAC Group Volume (R_k) and Surface Area (Q_k) Parameters

Main Group	Sub group	No.	R_k	Q_k	Sample Group Assignment	
24. "ACCl"	ACCl	51	1.1562	0.844	Benzene-chloro:	5 ACH, ACCl
25. "CNO_2"	CH_3NO_2 CH_2NO_2 $CHNO_2$	52 53 54	2.0086 1.7818 1.5544	1.868 1.560 1.248	Nitromethane: Propane-1-nitro: Propane-2-nitro:	1 CH_3NO_2 1 CH_3, 1 CH_2, 1 CH_2NO_2 2 CH_3, 1 $CHNO_2$
26. "$ACNO_2$"	$ACNO_2$	55	1.4199	1.104	Benzene-nitro:	5 ACH, 1 $ACNO_2$
27. "CS_2"	CS_2	56	2.0570	1.650	Carbon disulfide:	1 CS_2
28. "Furfural"	Furfural	57	3.1680	2.484	Furfural:	1 furfural
29. "Br"	Br	58	0.9492	0.832	Bromoethane:	1 CH_3, 1 CH_2, 1 Br
30. "C≡C"	CH≡C C≡C	59 60	1.2920 1.0613	1.088 0.784	Hexyne-1: Hexyne-2:	1 CH_3, 3 CH_2, 1 CH≡C 2 CH_3, 2 CH_2, 1 C≡C
31. "ACRY"	Acrylnitril	61	2.3144	2.052	Acrylnitrile:	1 Acrylnitril

Table M-4 : UNIFAC Group-Interaction Parameters for Highly Hydrophobic Systems

UNIFAC GROUP-INTERACTION PARAMETERS								
	1. CH_2	2. C=C	3. ACH	4. $ACCH_2$	5. OH	6. CH_3OH	7. H_2O	8. ACOH
1. CH_2	0.000	86.020	61.130	76.500	986.500	0.000	1318.000	1333.000
2. C=C	-35.360	0.000	38.810	74.150	524.100	0.000	270.600	526.100
3. ACH	-11.120	3.446	0.000	167.000	636.100	0.000	1039.218	1329.000
4. $ACCH_2$	-69.700	-113.600	-146.800	0.000	803.200	0.000	724.442	884.900
5. OH	156.400	457.000	89.600	25.820	0.000	0.000	-521.656	-259.700
6. CH_3OH	0.000	0.000	0.000	0.000	0.000	0.000	1200.875	0.000
7. H_2O	300.000	496.100	344.313	254.637	1316.838	-305.165	0.000	-844.211
8. ACOH	275.800	217.500	25.340	244.200	-451.600	0.000	-18.702	0.000
9. CH_2CO	26.760	42.920	140.100	365.800	164.500	0.000	-358.097	-133.100
10. CHO	505.700	56.300	23.390	106.000	-404.800	0.000	-477.415	n.a.
11. CCOO	114.800	132.100	85.840	-170.000	245.400	0.000	1014.559	-36.720
12. HCOO	90.490	-62.550	1967.000	2347.000	191.200	0.000	862.421	n.a.
13. CH2O	83.360	26.510	52.130	65.690	237.700	0.000	-314.700	n.a.
14. $(C)_2NH$	65.330	-28.700	-22.310	223.000	-150.000	0.000	-647.606	n.a.
15. $(C)_3N$	-83.980	-25.380	-223.900	109.900	28.600	0.000	-718.746	n.a.
16. $ACNH_2$	1139.000	2000.000	247.500	762.800	-17.400	0.000	-0.710	-253.100
17. Pyridin	-101.600	n.a.	31.870	49.800	-132.300	0.000	0.000	-341.600
18. CCN	24.820	-40.620	-22.970	-138.400	185.400	0.000	2.231	n.a.
19. COOH	315.300	1264.000	62.320	268.200	-151.000	0.000	-480.367	n.a.
20. CCl	91.460	97.510	4.680	122.900	562.200	0.000	1045.815	n.a.
21. CCl_2	34.010	18.250	121.300	140.800	747.700	0.000	930.813	n.a.
22. CCl_3	36.700	51.060	288.500	33.610	742.100	0.000	906.323	n.a.
23. CCl_4	0.000	0.000	0.000	0.000	0.000	0.000	-436.889	0.000
24. ACCl	-141.300	-158.800	-237.700	375.500	246.900	0.000	70.535	n.a.
25. CNO_2	-32.690	-1.996	10.380	-97.050	261.600	0.000	324.532	n.a.
26. $ACNO_2$	5541.000	n.a.	1824.000	-127.800	561.600	0.000	1034.369	n.a.
27. CS_2	0.000	0.000	0.000	0.000	0.000	0.000	826.571	0.000
28. Furfural	0.000	0.000	0.000	0.000	0.000	0.000	160.962	0.000
29. BR	-31.520	n.a.	506.300	27.430	524.900	0.000	n.a.	n.a.
30. C≡C	-72.880	41.380	n.a.	n.a.	n.a.	0.000	n.a.	n.a.
31. ACRY	0.000	0.000	0.000	0.000	0.000	0.000	1395.447	0.000

Table M-4 (Continued)

UNIFAC GROUP-INTERACTION PARAMETERS

	9. CH2CO	10. CHO	11. CCOO	12. HCOO	13. CH2O	14.(C)$_2$NH	15. (C)$_3$N	
1. CH$_2$	476.400	677.000	232.100	741.400	251.500	255.700	206.600	
2. C=C	182.600	488.880	37.850	449.100	214.500	163.900	61.110	
3. ACH	25.770	347.300	5.994	-92.550	32.140	122.800	90.490	
4. ACCH$_2$	-52.100	586.600	5688.000	115.200	213.100	-49.290	23.500	
5. OH	84.000	441.800	101.100	193.100	28.060	42.700	-323.000	
6. CH$_3$OH	0.000	0.000	0.000	0.000	0.000	0.000	0.000	
7. H$_2$O	679.678	1213.106	-111.583	35.885	540.500	1239.357	1131.329	
8. ACOH	-356.100	n.a.	-449.400	n.a.	n.a.	n.a.	n.a.	
9. CH$_2$CO	0.000	-37.360	-213.700	-38.470	-103.600	n.a.	-169.000	
10. CHO	128.000	0.000	-110.300	11.310	304.100	n.a.	n.a.	
11. CCOO	372.200	185.100	0.000	372.900	-235.700	-73.500	n.a.	
12. HCOO	70.420	35.350	-261.100	0.000	n.a.	n.a.	n.a.	
13. CH$_2$O	191.100	-7.838	461.300	n.a.	0.000	141.700	n.a.	
14. (C)$_2$NH	n.a.	n.a.	136.000	n.a.	-49.300	0.000	-189.200	
15. (C)$_3$N	225.300	n.a.	n.a.	n.a.	n.a.	865.900	0.000	
16. ACNH$_2$	-450.300	n.a.	-294.800	n.a.	n.a.	n.a.	n.a.	
17. Pyridin	-51.540	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	
18. CCN	-287.500	n.a.	-266.600	n.a.	38.810	n.a.	n.a.	
19. COOH	-297.800	n.a.	-256.300	312.500	-338.500	n.a.	n.a.	
20. CCl	286.300	-47.510	35.380	n.a.	225.400	n.a.	n.a.	
21. CCl$_2$	423.200	n.a.	-132.900	n.a.	-197.700	n.a.	-141.400	
22. CCl$_3$	552.100	242.800	176.500	488.900	-20.930	n.a.	-293.700	
23. CCl$_4$	0.000	0.000	0.000	0.000	0.000	0.000	0.000	
24. ACCl	128.100	n.a.	-246.300	n.a.	95.500	-108.400	1088.000	
25. CNO$_2$	-142.600	n.a.	129.300	n.a.	-94.490	n.a.	n.a.	
26. ACNO$_2$	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	
27. CS$_2$	0.000	0.000	0.000	0.000	0.000	0.000	0.000	
28. Furfural	0.000	0.000	0.000	0.000	0.000	0.000	0.000	
29. BR	-142.600	n.a.	24.370	n.a.	736.400	n.a.	n.a.	
30. C≡C	443.600	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	
31. ACRY	0.000	0.000	0.000	0.000	0.000	0.000	0.000	

Table M-4 (Continued)

UNIFAC GROUP-INTERACTION PARAMETERS								
	16ACNH2	17PYRI	18. CCN	19. COOH	20. CCl	21. CCl$_2$	22. CCl$_3$	23. CCl$_4$
1. CH$_2$	920.700	287.800	597.000	663.500	35.930	53.760	24.900	0.000
2. C=C	749.300	n.a.	336.900	318.900	204.600	5.892	-13.990	0.000
3. ACH	648.200	-4.449	212.500	537.400	-18.810	-144.400	-231.900	0.000
4. ACCH$_2$	664.200	52.800	6096.000	603.800	-114.100	-111.000	-12.140	0.000
5. OH	-52.390	170.000	6.712	199.000	75.620	-112.100	-98.120	0.000
6. CH$_3$OH	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
7. H$_2$O	-284.125	6.438	282.485	1061.387	288.644	336.083	318.549	1789.489
8. ACOH	119.900	-305.500	n.a.	n.a.	n.a.	n.a.	n.a.	0.000
9. CH$_2$CO	6201.000	165.100	481.700	669.400	-191.700	-284.000	-354.600	0.000
10. CHO	n.a.	n.a.	n.a.	n.a.	751.900	n.a.	-483.700	0.000
11. CCOO	475.500	n.a.	494.600	660.200	-34.740	108.900	-209.700	0.000
12. HCOO	n.a.	n.a.	n.a.	-356.300	n.a.	n.a.	-287.200	0.000
13. CH$_2$O	n.a.	n.a.	-18.510	664.600	301.100	137.800	-154.300	0.000
14. (C)$_2$NH	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.000
15. (C)$_3$N	n.a.	n.a.	n.a.	n.a.	n.a.	-73.850	-352.900	0.000
16. ACNH$_2$	0.000	n.a.	-281.600	n.a.	287.000	n.a.	n.a.	0.000
17. Pyridin	n.a.	0.000	-169.700	-153.700	n.a.	-351.600	-114.700	0.000
18. CCN	777.400	134.300	0.000	n.a.	88.750	-152.700	-15.620	0.000
19. COOH	n.a.	-313.500	n.a.	0.000	44.420	-183.400	76.750	0.000
20. CCl	429.700	n.a.	-62.410	326.400	0.000	108.300	249.200	0.000
21. CCl$_2$	n.a.	587.300	258.600	1821.000	-84.530	0.000	0.000	0.000
22. CCl$_3$	n.a.	18.980	74.040	1346.000	-157.100	0.000	0.000	0.000
23. CCl$_4$	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
24. ACCl	530.500	n.a.	356.900	n.a.	-314.900	n.a.	n.a.	0.000
25. CNO$_2$	n.a.	n.a.	0.283	n.a.	113.000	n.a.	n.a.	0.000
26. ACNO$_2$	134.900	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.000
27. CS$_2$	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
28. Furfural	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
29. BR	n.a.	n.a.	n.a.	5256.000	1169.000	n.a.	n.a.	0.000
30. C≡C	n.a.	n.a.	329.100	n.a.	n.a.	n.a.	n.a.	0.000
31. ACRY	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000

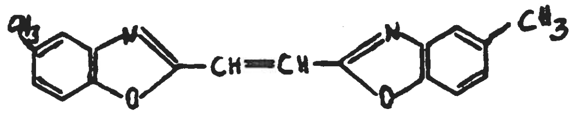
Table M-4 (Continued)

UNIFAC GROUP-INTERACTION PARAMETERS								
	24. ACCl	25. CNO_2	26.$ACNO_2$	27. CS_2	28.FUR	29. Br	30. C≡C	31. ACRY
1. CH_2	321.500	661.500	543.000	0.000	0.000	479.500	298.900	0.000
2. C=C	393.100	357.500	n.a.	0.000	0.000	n.a.	31.140	0.000
3. ACH	538.200	168.000	194.900	0.000	0.000	-107.300	n.a.	0.000
4. $ACCH_2$	-126.900	3629.000	4448.000	0.000	0.000	318.500	n.a.	0.000
5. OH	287.800	256.500	157.100	0.000	0.000	202.100	n.a.	0.000
6. CH_3OH	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
7. H_2O	959.729	223.478	340.363	765.590	116.395	n.a.	n.a.	92.250
8. ACOH	n.a.	n.a.	n.a.	0.000	0.000	n.a.	n.a.	0.000
9. CH_2CO	174.500	137.500	n.a.	0.000	0.000	245.200	-246.600	0.000
10. CHO	n.a.	n.a.	n.a.	0.000	0.000	n.a.	n.a.	0.000
11. CCOO	629.000	-81.130	n.a.	0.000	0.000	18.880	n.a.	0.000
12. HCOO	n.a.	n.a.	n.a.	0.000	0.000	n.a.	n.a.	0.000
13. CH_2O	66.150	95.180	n.a.	0.000	0.000	-202.300	n.a.	0.000
14. $(C)_2NH$	4350.000	n.a.	n.a.	0.000	0.000	n.a.	n.a.	0.000
15. $(C)_3N$	-86.360	n.a.	n.a.	0.000	0.000	n.a.	n.a.	0.000
16. $ACNH_2$	287.900	n.a.	-139.300	0.000	0.000	n.a.	n.a.	0.000
17. Pyridin	n.a.	n.a.	n.a.	0.000	0.000	n.a.	n.a.	0.000
18. CCN	52.310	-0.515	n.a.	0.000	0.000	n.a.	-203.000	0.000
19. COOH	n.a.	n.a.	n.a.	0.000	0.000	-95.000	n.a.	0.000
20. CCl	464.400	32.730	n.a.	0.000	0.000	-125.900	n.a.	0.000
21. CCl_2	n.a.	n.a.	n.a.	0.000	0.000	n.a.	n.a.	0.000
22. CCl_3	n.a.	n.a.	n.a.	0.000	0.000	n.a.	n.a.	0.000
23. CCl_4	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
24. ACCl	0.000	-154.500	n.a.	0.000	0.000	-60.700	n.a.	0.000
25. CNO_2	794.400	0.000	533.200	0.000	0.000	10.170	-27.700	0.000
26. $ACNO_2$	n.a.	-85.120	0.000	0.000	0.000	n.a.	n.a.	0.000
27. CS_2	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
28. Furfural	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
29. Br	224.000	125.300	n.a.	0.000	0.000	0.000	n.a.	0.000
30. C≡C	n.a.	174.400	n.a.	0.000	0.000	n.a.	0.000	0.000
31. ACRY	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000

Appendix D Substance data for model exercise

No: 1

Formula:



MW = 290 g/mol

Melting point (°C): 183 Boiling point (°C):

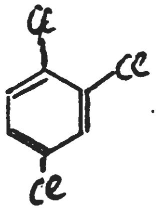
Vapour pressure
(Pa, 20°C): 10^{-4} Water solubility (mg/l): 6.6×10^{-3}

log Pow: 5.72 k deg (h^{-1}): 0.05 t1/2 (days): 0.57

use: household, optical brightener for detergents

No: 2

Formula:



MW = 181.45 g/mol

Melting point (°C): 17 Boiling point (°C): 214

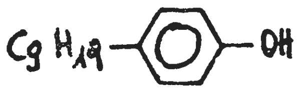
Vapour pressure
(Pa, 20°C): 38 Water solubility (mg/l): 32

log Pow: 4.01 k deg (h^{-1}): 10^{-4} t1/2 (days): 288

use: volatile agent in textile finishing

No: 3

Formula:



MW = 220 g/mol

Melting point (°C):-8 Boiling point (°C): 175 - 188

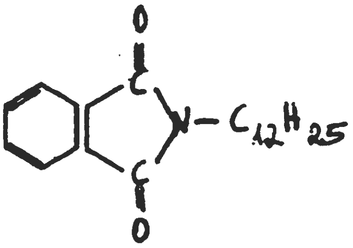
Vapour pressure
(Pa, 20°C): 0.05 - 0.17 Water solubility (mg/l): 6.4

log Pow: 6.1 k deg (h^{-1}): 10^{-4} t1/2 (days): 288

use: laundry detergent`s degradation product

No: 4

Formula:



MW = 315 g/mol

Melting point (°C): 61

Boiling point (°C): 350

Vapour pressure (Pa, 20°C): 2×10^{-5}

Water solubility (mg/l): $1.9 - 10^{-3}$

log Pow: 7.3

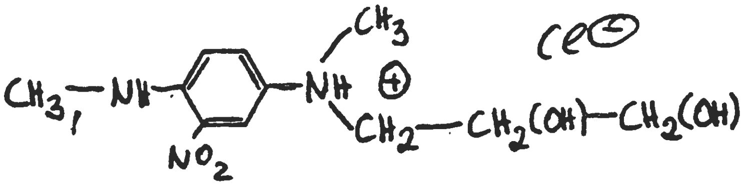
k deg (h^{-1}): 10^{-4}

t1/2 (days): 288

<u>use</u>: disperse dye - additive textile finishing

No: 5

Formula:



MW = 291.74 g/mol

Melting point (°C): 170

Boiling point (°C):

Vapour pressure (Pa, 20°C): 96.5

Water solubility (mg/l): 214×10^3

log Pow 1.09

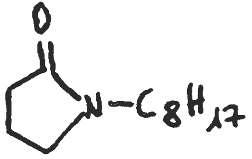
k deg (h^{-1}): 2.6×10^{-4}

t 1/2 (days): 111

<u>use</u>: dye in cosmetics

No: 6

Formula:



MW = 197.3 g/mol

Melting point (°C): 17

Boiling point (°C): 292

Vapour pressure (Pa, 20°C): 7.1×10^{-2}

Water solubility (mg/l): 51

log Pow: 3.27

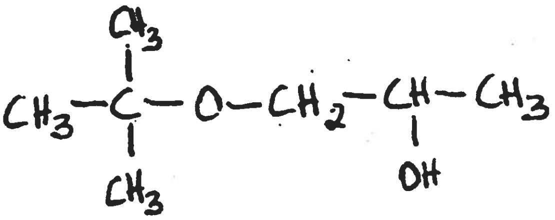
k deg (h^{-1}): 1.7×10^{-3}

t1/2 (days): 16.8

<u>use</u>: household, shampoo additive

No: 7

Formula:



$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-O-CH_2-\underset{OH}{CH}-CH_3$

MW = 132.2 g/mol

Melting point (°C):

Boiling point (°C): 154

Vapour pressure (Pa, 20°C): 374

Water solubility (mg/l): 188×10^3

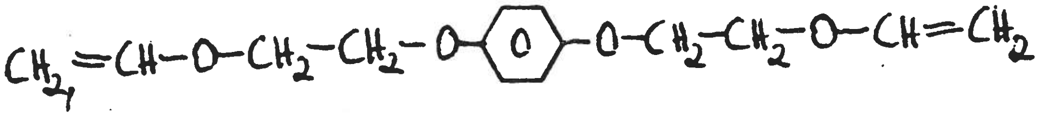
log Pow: 0.73

k deg (h^{-1}): 10^{-4} t1/2 (days): 288

<u>use</u>: household cleaning agent

No: 8

Formula:



MW = 250.3 g/mol

Melting point (°C): 105

Boiling point (°C):

Vapour pressure (Pa, 20°C): 3.2×10^{-5}

Water solubility (mg/l): 0.69

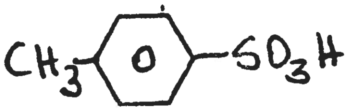
log Pow: 2.8

k deg (h^{-1}): 10^{-4} t1/2 (days): 288

<u>use</u>: paperchemical: additive thermopaper

No: 9

Formula:



MW = 172.2 g/mol

Melting point (°C): 38

Boiling point (°C):

Vapour pressure (Pa, 20°C): 1

Water solubility (mg/l): 670 000

log Pow: 0.78

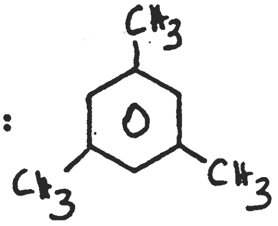
k deg (h^{-1}): 1.2×10^{-3}

t1/2 (days): 23

<u>use</u>: Intermediate

No: 10

Formula:



MW = 120.2 g/mol

Melting point (°C):

Boiling point (°C): 164.7

Vapour pressure (Pa, 20°C): 248

Water solubility (mg/l): 20

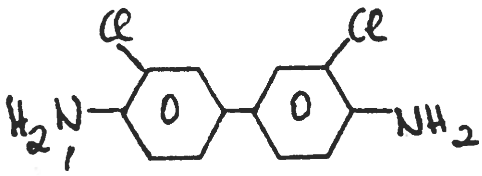
log Pow: 3.8

k deg (h^{-1}): 10^{-4} t1/2 (days): 288

<u>use</u>: Intermediate

No: 11

Formula:



MW = 253.1 g/mol

Melting point (°C): 136

Boiling point (°C):

Vapour pressure (Pa, 20°C): 6×10^{-7}

Water solubility (mg/l): 3.11

log Pow: 3.5

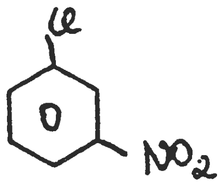
k deg (h^{-1}): 5×10^{-4}

t1/2 (days): 56

<u>use</u>: Intermediate

No: 12

Formula:



MW = 157.5 g/mol

Melting point (°C): 44.5

Boiling point (°C): 236

Vapour pressure (Pa, 20°C): 1.1

Water solubility (mg/l): 390

log Pow: 2.46

k deg (h^{-1}): 10^{-4} t1/2 (days): 288

<u>use</u>: Intermediate

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