Status and Results of the Group Contribution Methods

UNIFAC and Modified UNIFAC (Dortmund)

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From UNIFAC to Mod. UNIFAC (Dortmund)

The primary intention developing the original UNIFAC method was the reliable prediction of VLE-data for distillation processes.

Because of some weakness of original UNIFAC, Modified UNIFAC (Dortmund) was introduced. Improved results for various kinds of mixture data (VLE, $h^f$, SLE, $\gamma$, LLE, $cP$, azeotropic data) are obtained by simultaneous fitting of temperature dependent group interaction parameters to the mentioned types of thermodynamic data, which cover a large temperature range.

Source of the experimental data are the Dortmund Data Bank (DDB), systematic measurements and confidential data placed at our disposal by the members of the UNIFAC consortium.

The superiority of Modified UNIFAC (Dortmund) compared to other group contribution methods is shown in figure 1:

![Fig. 1 Mean deviations between experimental and calculated VLE-data](data:image/png;base64,iVBORw0KGgoAAAANSUhEUgAAANAAAAAkwCAIAAABQ3QyAAAABGdBTUEAALGPC/xhB蒋AAAAABJRU5ErkJggg==)

However, Modified UNIFAC (Dortmund) and UNIFAC are very valuable tools for the design, synthesis and optimization of separation processes and other applications of industrial interest:

- **Fig. 2 Different Applications of group contribution methods**

The UNIFAC consortium

In 1996 a company consortium was founded to support the further development of both models. Nowadays, this consortium consists of more than 30 companies:

- **Fig. 3 Members of the UNIFAC consortium**

The current parameter matrices of both models symbolize the progress made in recent years:

- **Fig. 4 Current Modified UNIFAC (Dortmund) parameter matrix**

However, Modified UNIFAC (Dortmund) and UNIFAC are very valuable tools for the design, synthesis and optimization of separation processes and other applications of industrial interest:

- **Fig. 5 Current UNIFAC parameter matrix**

The new or revised parameters obtained within the consortium are exclusively available for the sponsors and cannot be obtained by other sources (e.g. commercial process simulators like ASPEN Plus® or ChemCAD®).

The latest progress of the research work is available via internet:

[www.uni-oldenburg.de/tchemie/consortium](http://www.uni-oldenburg.de/tchemie/consortium)

**Main objectives of the research work**

- extensive examination of the current parameter matrices (Figures 4 + 5)
- revision of existing parameters using the Dortmund Data Bank (DDB)
- extension of the parameter matrices for both methods
- introduction of new, more flexible structural groups
- investigations considering reactive systems
- determination of selective solvents for extractive distillation and extraction processes
- consideration and overcome of weaknesses like proximity and isomeric effects

The following figure gives an impression of the ability of Modified UNIFAC (Dortmund) to predict simultaneously different kinds of thermodynamic mixture data:

- **Fig. 6 Typical results for the system ethanol (1) + benzene (2)**
  - : experimental data
  - : Modified UNIFAC (Dortmund)