

## CHALLENGES IN THERMODYNAMICS

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### ABSTRACT

An examination of the program of the next meeting of distillation and absorption indicates there are only a few lectures on thermodynamics. The authors asked some important companies to give their view of the trends in thermodynamics.

This plenary lecture concerns some of the remaining challenges in the thermodynamics related to distillation:

- data banks and locations for measuring experimental data
- new solvents for extractive distillation
- reacting systems
- a priori prediction of thermodynamic properties

Recent theoretical advances provide benefits that should encourage engineers to switch from activity-coefficient models to equations of state.

## TRENDS AND CHALLENGES IN THERMODYNAMICS

Vision 2020 [39] summarizes the directions of distillation and absorption.

New technologies compete with distillation. Vision 2020 balances distillation and absorption as follows: "Under these conditions adsorbents might displace energy intensive cryogenic distillation and liquefaction systems and displace distillation as a separation technology in application where reflux ratios greater than 10:1 are required."

About distillation itself, Vision 2020 says that " it is considered to be a mature technology and is often the separation technology of choice because of its well-understood nature."

Are there goals achievable? Vision 2020 identifies significant barriers such as understanding of fluid flow, foaming and frothing and the lack of effective sensors for large distillation columns. Common complaint is that there is a general lack of both sponsors and mentors in the field and that the number of international ranked experts in the field of both -thermodynamics and distillation- is declining sharply.

Yes, there are goals to reach but there is only one in thermodynamics: enhance relative volatilities.

The assessment of the authors of this article is to show that a lot of computational work is possible with complicated but readily accessible models. We want to show that the authors of Vision 2020 have forgotten prediction of thermophysical properties. In addition we will demonstrate that the experimental problems concerning reactive distillation appear to be solved.

For this conference, the authors have asked some prominent thermodynamicists from larger companies about their opinion of the role of thermodynamics in distillation.

### The view of a specialty company.

At present and in the future, our job is to find the purification route for a complex compound from a mixture of side products. Complex means a molecule having more than one functional group and a molar mass above 100 amu. Typical distillations will be performed at about 150°C and vacuum. The purification route has to be known within a year (with 1 kg of pre-product) and the production has to be in an existing plant (multi-purpose plant). Thus we apply predictive models like COSMO-RS, Unifac(Do) to find difficult close boilers and azeotropes. The process will not run at room temperature but somewhere between 100-200°C. Both models suffer inaccuracies at this level.

It would be helpful to improve the quality of the methods for higher temperatures. Also we need methods for accurate vapor pressure estimation methods that can distinguish between isomers. An alternative is that analytic equipment becomes available to measure small amounts of material at a high through-put.

Thermodynamics plays also an essential role in the synthesis of biomolecules at high pressure ( $P > 50$  bar,  $T < 150^\circ\text{C}$ ). Especially for gases like  $\text{CO}_2$  we wish to have tools that calculate the entire phase diagram for SLE-LLE-VLLE-GLE.

## The view of an international chemical and pharmaceutical company

We found that small errors can cause big effects in the separation equipment. Thermodynamics is the basis for understanding transport phenomena. Thermodynamics should produce predictive methods for all kinds of thermophysical properties.

## The view of an engineering company

We are convinced that thermodynamics remains as one of the cornerstones of chemical engineering.

All over the chemical engineering world, thermodynamics seems to be on the decline. That is, in part, our own fault because we have not given sufficient attention (in our courses, publications, technical meetings, etc.) to show how and why thermodynamics is important not only for conventional but also for modern (high-tech) chemical engineering.

Thermodynamics serves as the integrating factor for chemical engineering sciences. We complain that thermodynamics is not standardized: there are no accepted recommendations for what  $G^E$ -model and what EOS should be used with what parameters. There is still a lack of compatibility:  $h^E$  to activity coefficients, LLE to VLE, infinite dilution to finite dilution and vice versa.

We would like to apply EOS but there are too many models. We miss mixture rules for density, viscosity, surface tension and heat conductivity. We find excess volumes for binary mixtures and do not know how to extrapolate to multicomponent mixtures.

Universities tend to publish correlations and models restricted to special applications without testing general applicability. They do not program in the rules of CAPE.

We need predictive methods for the first guess and for non-important traces of components. Real predictive methods do not pay back their implementation compared to structure-interpolating methods. In the end, we only trust measurements.

We predict that the description of complex mixtures (electrolytes, polymers, special substances like formaldehyde) becomes more important.

We are looking forward to activities in Germany to step into the area of biotechnology. Data banks for this kind of data are missing. We face new problems: bacteria as reactors, products, catalysts and solid products. This is a challenge for simulation programs.

This lecture excludes electrolytes because they do not play an important role in distillation except for absorption where powerful methods, especially for  $\text{CO}_2$  or  $\text{NH}_3$  in water or in aqueous electrolyte solutions are available from the work of Maurer in Kaiserslautern, Germany.

## DATA BANKS

As explained in chapter 5.2.1, the development of huge data banks was the key for the development of structure-interpolating methods. The main European databank is DETHERM (**DE**chema **THERM**ophysical Property Databank) which is a joint venture between Dechema in Frankfurt and Fachinformationszentrum (FIZ) Chemie in Berlin, both in Germany. DETHERM consists of

- DDB (Dortmund Data Bank), initiated by Onken and built up by Gmehling and co-workers; DDB was published in the famous Dechema Chemistry Data Series
- ELDAR (Electrolyte Data Regensburg), initiated and built up by Barthel in Regensburg, Germany
- internal databanks by the former east-German companies "Sächsische Olefinwerke" and "Leuna Werke"
- CDATE by Matous in Prague
- in-house data banks by FIZ Chemie and Dechema

Detherm consists of more than 900,000 data sets including 25,000 substances and a maximum of 73 properties; it is the world's largest data bank. Detherm is available with many process calculators like AspenPlus®.

Several projects have been initiated to extend the contents of Detherm like DDB-pure, where all available pure component data was input by groups in Oldenburg (Germany), Prague (Czech Republic), Graz (Austria), Minsk (Belarus), Tallinn (Estonia) and Berlin (Germany). Detherm is currently being extended by DDBST GmbH (a company based in Oldenburg), DECHEMA e.V., FIZ CHEMIE Berlin and the University of Regensburg.

Detherm can be obtained from internet (<http://i-systems.dechema.de/detherm/>). Special offers are given to universities.

Even in smaller countries like Germany the locations of laboratories available to measure data are not completely known. In 1997, the head of the Dechema working party "engineering data" W.Arlt, started a project that collected the available apparatus for thermophysical properties in universities and government institutions in Germany (see Fig. 2.1). These references are available in German from: <http://argon.dechema.de/internet/dechema/infsys/publi/deutsch/katalogmessmoeglichkeiten/inhalt.htm>.

It comprises

- phase equilibrium (VLE, LLE, SLE, GLE, vapour pressure, ...)
- densities, and PVT
- calorimetric data
- transport properties like viscosity, thermal conductivity, diffusion
- surface tension
- optical and electrical properties

The working party plans to extend this reference to Europe and to issue the current booklet as an on-line searchable file in English.



# **Katalog Meßmöglichkeiten für thermophysikalische und verwandte Daten**

**Herausgegeben vom  
Arbeitsausschuß "Ingenieurdaten"  
der DECHEMA**

**1.Auflage**

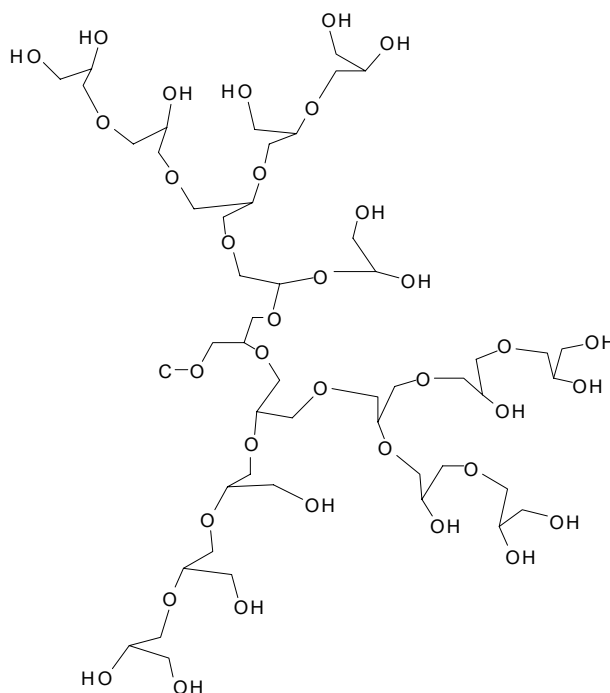
*Fig 2.1.: booklet issued by the Dechema working party "engineering data" comprising the possibilities to measure thermophysical data in Germany*

## INNOVATIVE COMPOUNDS

Ionic Liquids (IL) and Hyperbranched Polymers (HyP) represent comparatively new substances, which, due to their unique structures and properties, are promising components for a wide variety of applications. Here, only the application as an extractive solvent in distillation is discussed. For more detail refer to Seiler [32].

### Hyperbranched Polymers as extractive solvents

Due to their unique structures and properties, highly branched, three-dimensional polymers such as Dendrimers or Hyperbranched Polymers, attract increasing attention. Dendrimers are perfectly branched macromolecules with a degree of branching (DB) of 1.0, which are only accessible by time-consuming multi-step synthesis. An economically interesting alternative are the randomly branched Hyperbranched Polymers, which can easily be produced on large scale by a one-step polymerization of appropriate  $AB_2$  monomers. The thermal, mechanical or solution properties can be tailored via the number and the nature of the functional groups. A Hyperbranched Polymer is shown in Fig. 3.1.1.



*Fig. 3.1.1: hyperbranched poly-Glycerol*

### Ionic liquids

Although the first IL was synthesized in 1914 [40] [34] research activities on these compounds increased dramatically with the development of the first air- and moisture-stable IL in 1992 and with the commercial availability of IL by various

suppliers, among them in 1999 by the small German start-up company "Solvent Innovation".

An IL has no effective vapor pressure, has a relatively low viscosity, is thermally stable up to 200 °C, has a liquid range of about 300 K and is a good solvent for a wide range of organic, inorganic and polymeric materials. Moreover an IL is much less corrosive than a conventional high-melting salt. Due to their properties, IL's are serious candidates for solvents in several industrial processes.

Common anions are shown in Fig. 3.2.1, common cations in Fig. 3.2.2 .

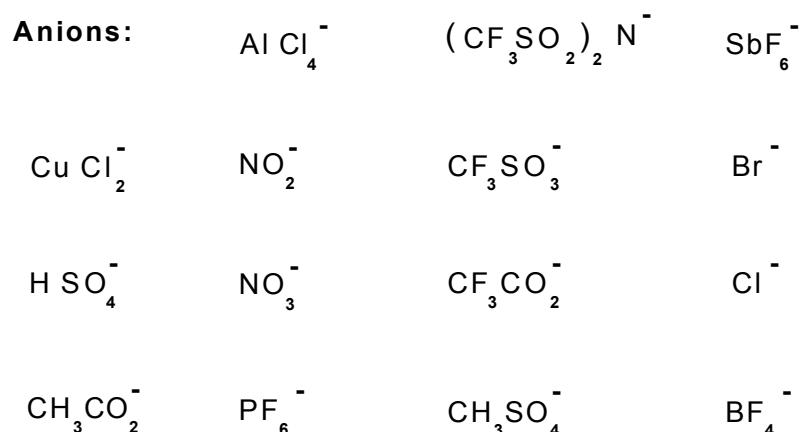


Fig. 3.2.1: some common anions in Ionic Liquids

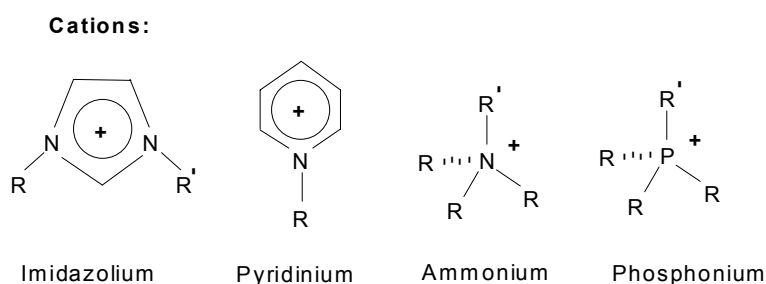


Fig. 3.2.2: some common cations in Ionic Liquids

Choice of the cation and the anion allows us to tailor thermophysical properties. Fig 3.2.3 shows the liquid-liquid equilibrium of Butanol-bmimPF6 (1-n-butyl-3-methyl-imidazolium hexafluorophosphate, C<sub>8</sub> H<sub>15</sub> F<sub>6</sub> N<sub>2</sub> P). The calculated line comes from the à priori predictive method COSMO-RS (see chapter 5.3). COSMO-calculations were performed with each ion to obtain the screening charge energy (Fig. 3.2.4). The molecule is constructed as the sum of the two parts. No special ionic G<sup>E</sup>-model is used. The figure shows that the liquid-liquid phase splitting is predicted reasonably. Structure-interpolating methods cannot predict the properties of IL's.

No other prediction method is known to the authors to predict for this type of compound.

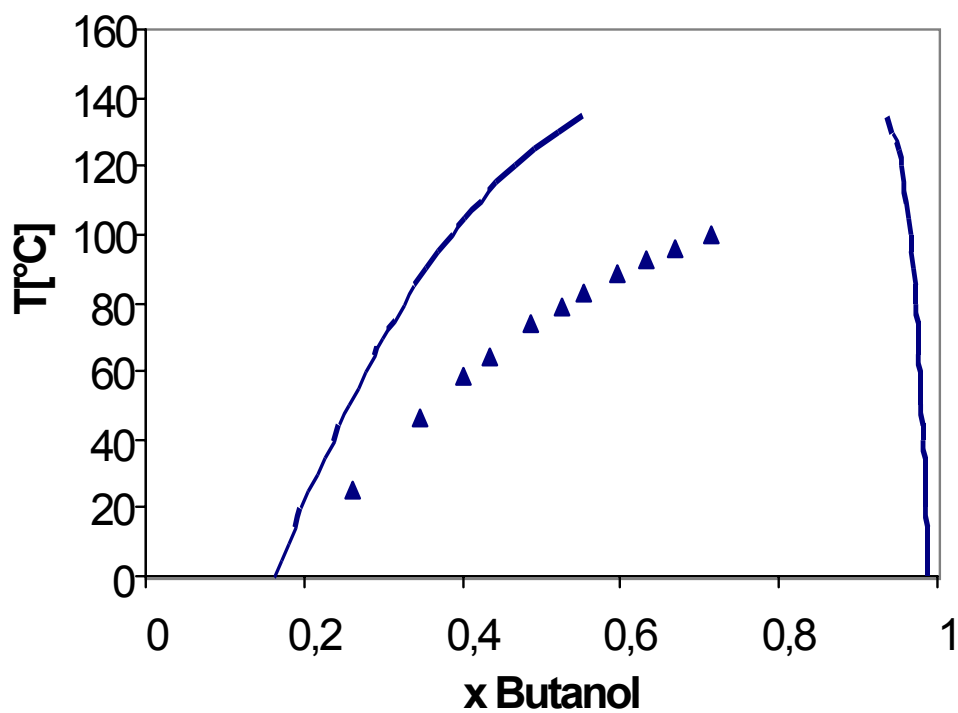


Fig. 3.2.3: LLE of Butanol-bmimPF6 (1-n-butyl-3-methylimidazolium hexafluorophosphate, C<sub>8</sub> H<sub>15</sub> F<sub>6</sub> N<sub>2</sub> P): exp. data (mol fraction) by Wu [43], calculations with COSMO-RS. This figure is from [9].



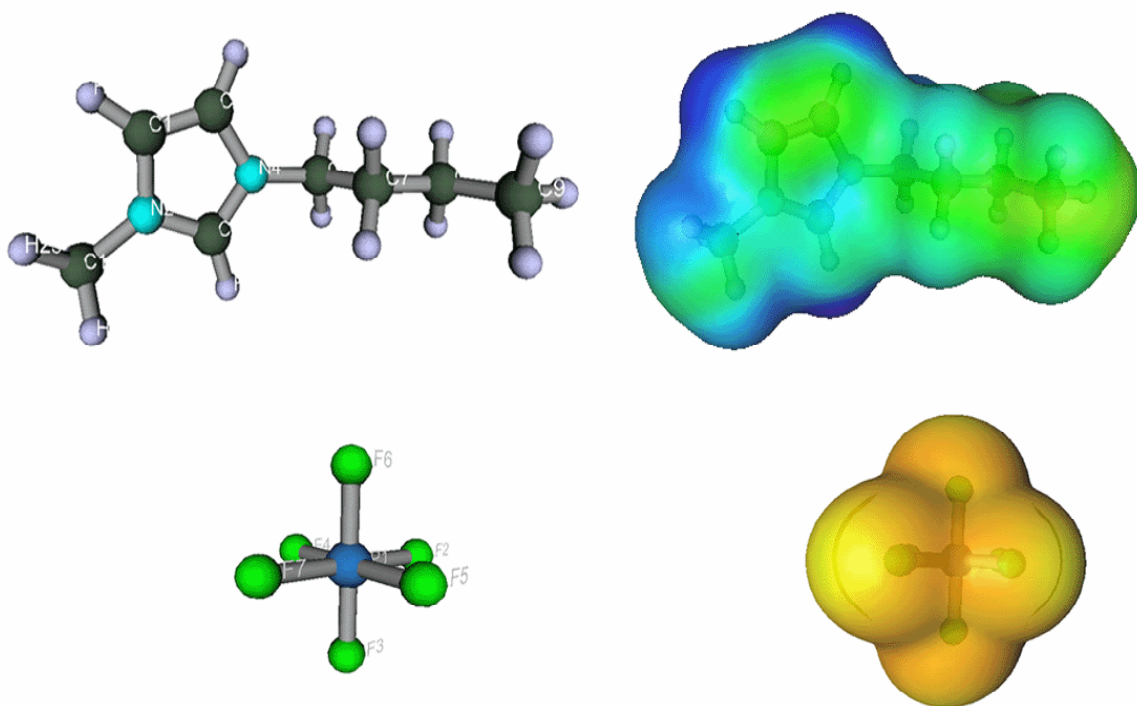


Fig 3.2.4: Structures of the ions of  $bmim PF_6$ : structural formula and screening charge density on the surface by COSMO (cation at top, anion in the bottom row).

### **Use of Ionic Liquids (IL's) and Hyperbranched Polymers (HyP) as extractive solvents**

Separation factors are determined by measuring ternary vapor-liquid equilibria (head space analysis) of azeotropic or close boiling systems in the presence of different amounts of IL or HyP. As an example, the separation of ethanol-water was chosen, where it is known that IL's break nearly all azeotropes [3] [4].

From the many possible IL's EMIM-BF<sub>4</sub> was chosen because it was available from the company "Solvent Innovation". Reliable binary data are available from Pemberton [26].

As can be seen from Fig. 3.3.1, only 10 mol% of this IL is required to break the azeotrope. A separation factor with practical application is reached with 30 mol%. The results are taken from Seiler et al. [32].

Similar results were obtained with Hyperbranched Polymers. Looking at Fig. 3.1.1, their structure is similar to a huge ethanediol molecule. The idea was that breaking the azeotrope should work with OH-groups contained within a polymer.

The result is depicted in Fig. 3.3.2. Polyglycerol had molar masses of 1400 and 4000 g/mol, respectively. Both polymers were able to break the azeotrope at concentrations higher than 20 mass%. The results are taken from Seiler et al. [33]

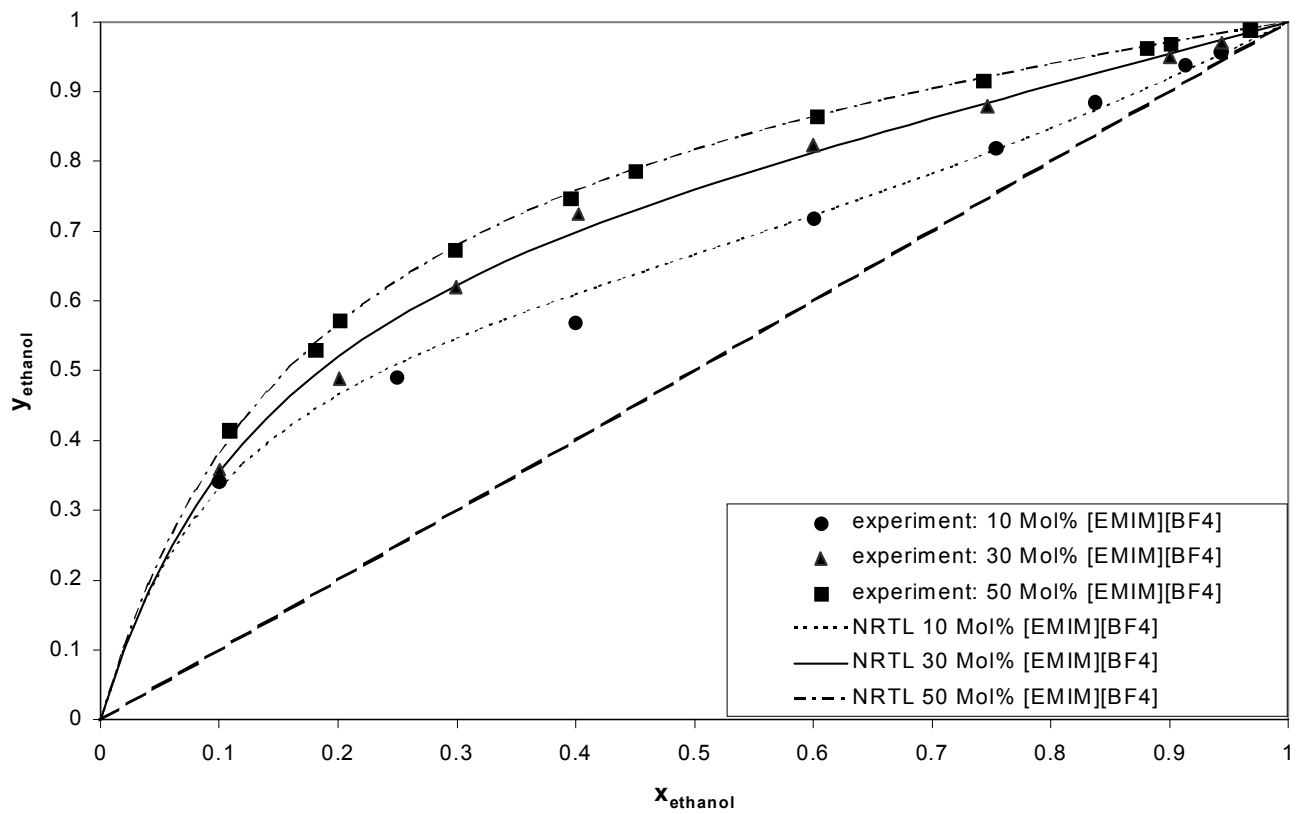


Fig. 3.3.1: . Experimental VLE-data for the system Ethanol–Water–[EMIM][BF<sub>4</sub>] (1-Ethyl-3-methylimidazolium tetrafluoroborate) and calculated VLE-curves using NRTL for 10 mol%, 30 mol% and 50 mol% IL at  $T_{\text{equilibrium}} = 90\text{ }^{\circ}\text{C}$

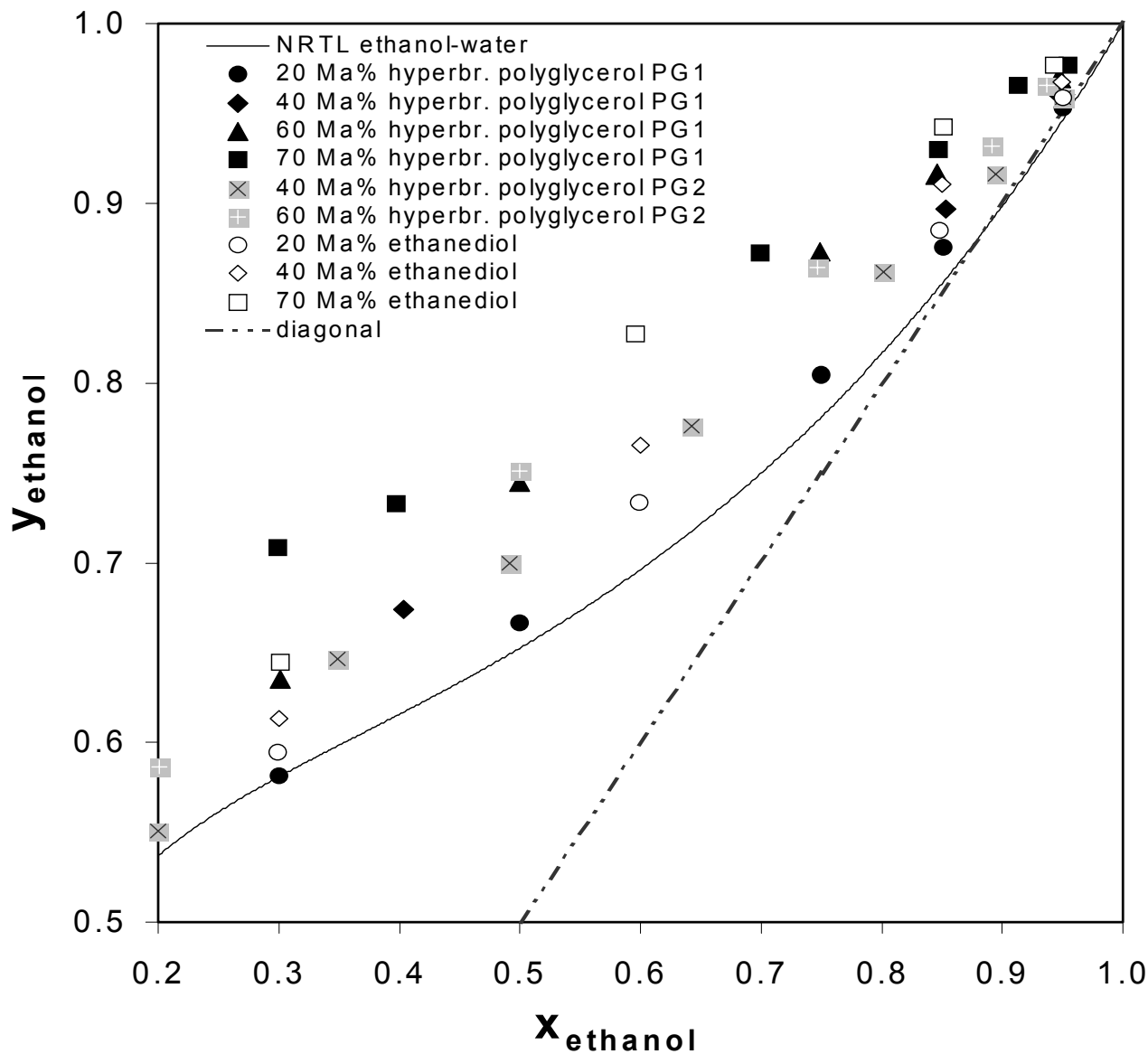


Fig. 3.3.2 Experimental VLE results for the system hyperbranched poly Glycerol–Ethanol–Water and 1,2-Ethanediol–Ethanol–Water for different polymer and Ethanediol concentrations at 90 °C; hyperbranched poly Glycerol PG1:  $M_n=1400$  g/mol,  $M_w/M_n=1.5$ ; hyperbranched poly Glycerol PG2:  $M_n=4000$  g/mol,  $M_w/M_n=2.1$ ;

What are the advantages of both compounds?

First, the azeotropes are broken at extractive solvent levels lower than ethanediol. Thus, the liquid molar load in the column is reduced.

Further, no rectifying section is needed above the extractive solvent feed, because the vapour pressure of both compounds is close to zero.

Last, the recovery of the extractive solvent does not need a distillation column but a simple evaporator. The heat duty of the reboiler is cut to 50%.

What is unresolved?

The availability of both extractive solvents is not completely solved, but other applications make it probable. Other properties like long-term stability, toxicity, storage and corrosion must be investigated.

In total, 2 new classes of solvent are on the way toward application in chemical engineering. For more details related to Hyperbranched Polymers refer to Seiler [33].

## REACTIVE SYSTEMS

One of the last unresolved problems is the determination of vapor-liquid equilibria in reacting systems. If we assume the simplest case (Alcohol+Acid to Ester + Water), the binary interaction parameters of the non-reacting species (i.e. Acid-Water) are easily determined. If one tries to determine the VLE data of the Alcohol-Acid mixture, a 4-component mixture (in this simple case) is formed immediately. The only way to determine parameters for  $G^E$ -models seems to be to wait for the state of chemical equilibrium [22]. Then the binary interaction parameters can be fitted to the four-component system using the pre-determined parameters for the other binaries. With a reliable theory, this procedure should work. In reality, because all models show a more or less pronounced intercorrelation of the interaction parameters, the result is somewhat undetermined. Because of this reason, several approaches have been made to "measure" the reacting system's VLE.

The application is quite obvious. In reactions of a certain half-time interval (some 10 minutes to few hours), reactive distillation columns are the choice instead of reactors plus separation. The earliest publication concerning the concept of reactive distillation was given by Backhaus [5]. In distillation columns, chemical equilibrium tells us, that if the products are distilled off the reaction zone, nearly complete (depending on the reaction rate) conversion can be achieved. In very fast reactions, (tube) reactors are advantageous, in very slow reaction the residence time in distillation columns is too small.

Reactive distillation columns use the enthalpy of reaction in situ, i.e. without heat transfer problems. From a thermodynamical point of view the loss of exergy is reduced.

Often, reacting mixtures show an azeotrope. It is possible to overcome such azeotropes in reactive systems. For further details, refer to Arlt [2].

### Apparatus and procedures

#### Chemical equilibrium

Lee [22] used an Othmer still to determine the VLE at chemical equilibrium (CE). This (Fig. 4.1) cell works with the principle of circulation. The pressure is kept constant. Liquid and vapor concentrations were determined at chemical equilibrium at different

constant temperatures. A gas chromatograph was used for analysis. To regress the data, the UNIQUAC and WILSON model were utilized considering the the vapour phase association of the acid.

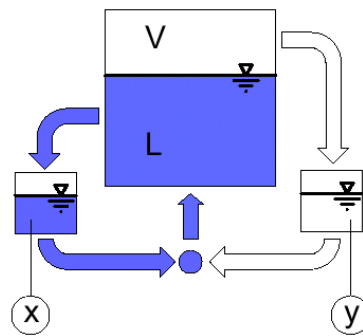


Fig. 4.1: Experimental set-up by Lee (1996)

#### Fast determination of VLE

Pöpken et al. [29] use a computer-operated static apparatus (Fig. 4.2). They measured isothermal P-x data of the binary systems required for the methyl acetate production process. A presumption for these measurements is that the VLE is established much faster than chemical equilibrium which yields operating temperatures up to 323.15 K.

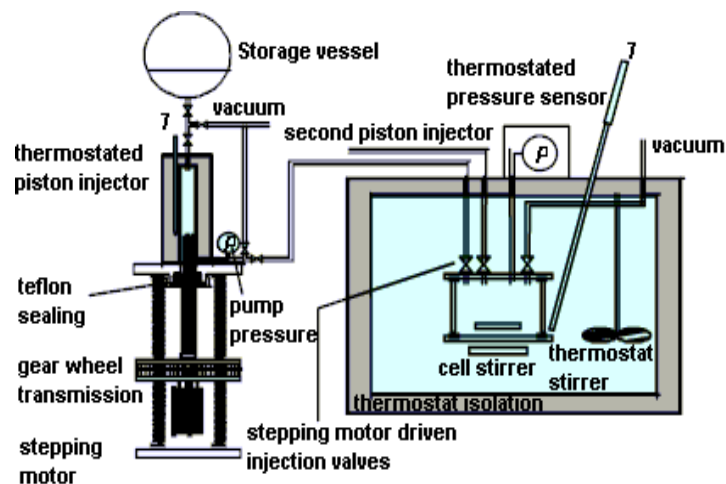


Fig.4.2: Static apparatus by Pöpken [22]

Roederer et al. [30] investigated an isomeric reaction ( $\alpha$ - and  $\beta$ -isophorone) at 388, 423 and 493 K. They experimented in a stirred batch reactor in the form of a closed loop reactor (Fig. 4.3). For VLE experiments it was possible to use the experimental set-up as a flow type cell. The compositions of the phases are obtained on-line with a Fourier-transform-infrared-spectrometer. The feed of the set-up is stored as a mixture of the components. The reaction takes place only with a catalyst. The reaction is neglected during the VLE measurements.

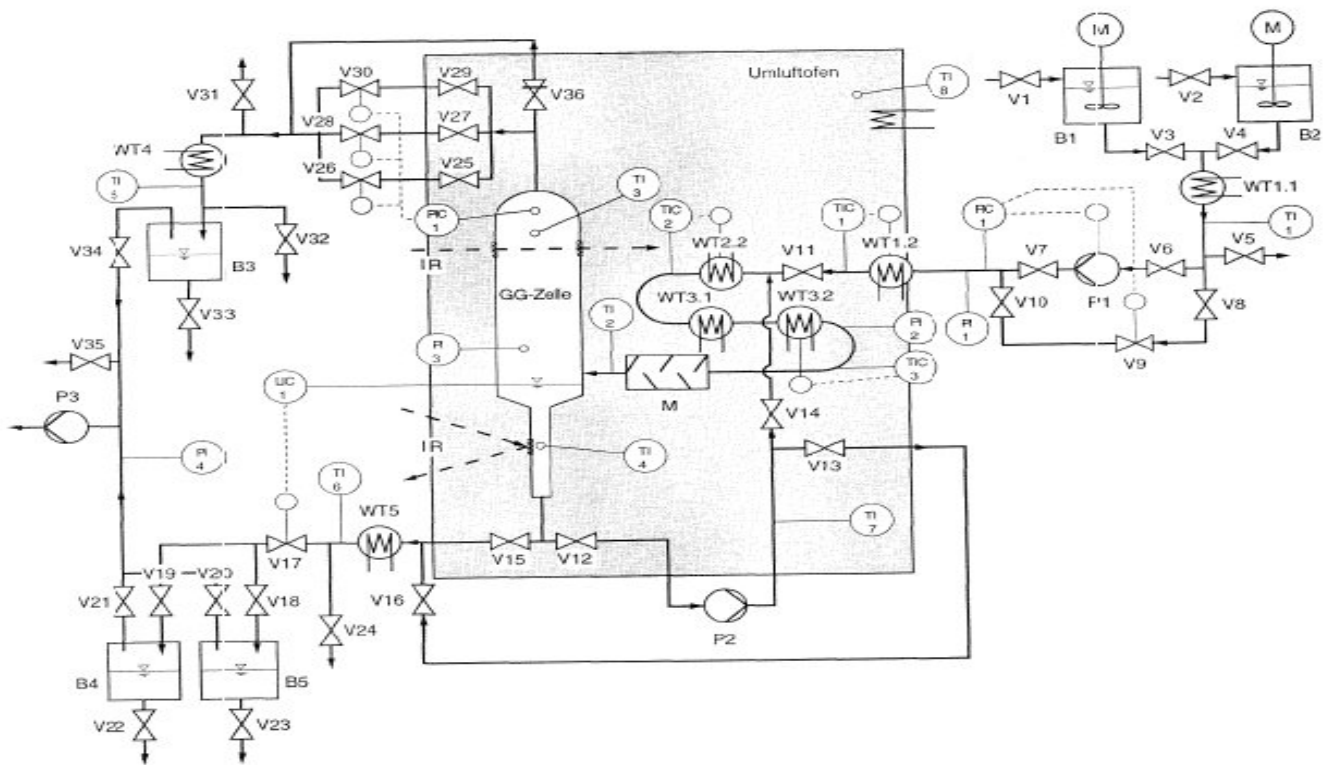


Fig. 4.3.: Experimental setup by Roederer [30]

Alsmeyer et al. [1] have set up a flow-through apparatus for VLE measurements in reactive systems which also allow determination of reaction kinetics in the liquid phase (Fig. 4.4). The reactive mixture is forced into a steady state which does not represent its chemical equilibrium but reaches phase equilibrium between vapor and liquid. Both phases are then analyzed in situ by mid-infrared (MIR) spectroscopy. While the gas phase is measured by transmission, attenuated total reflection (ATR) is used for the liquid phase measurements.

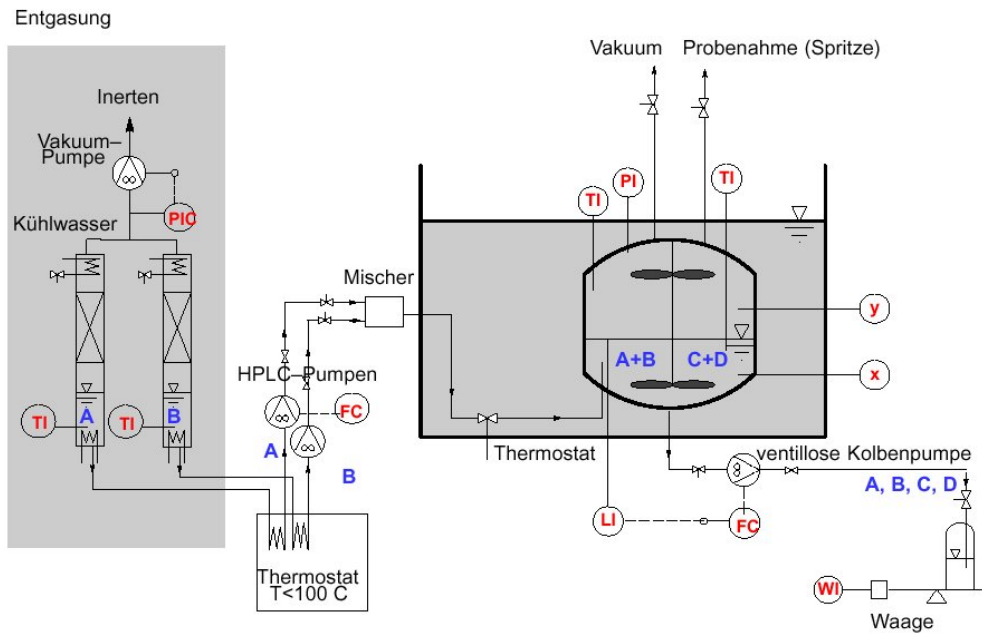


Fig. 4.4: experimental set-up by Alsmeyer [1]

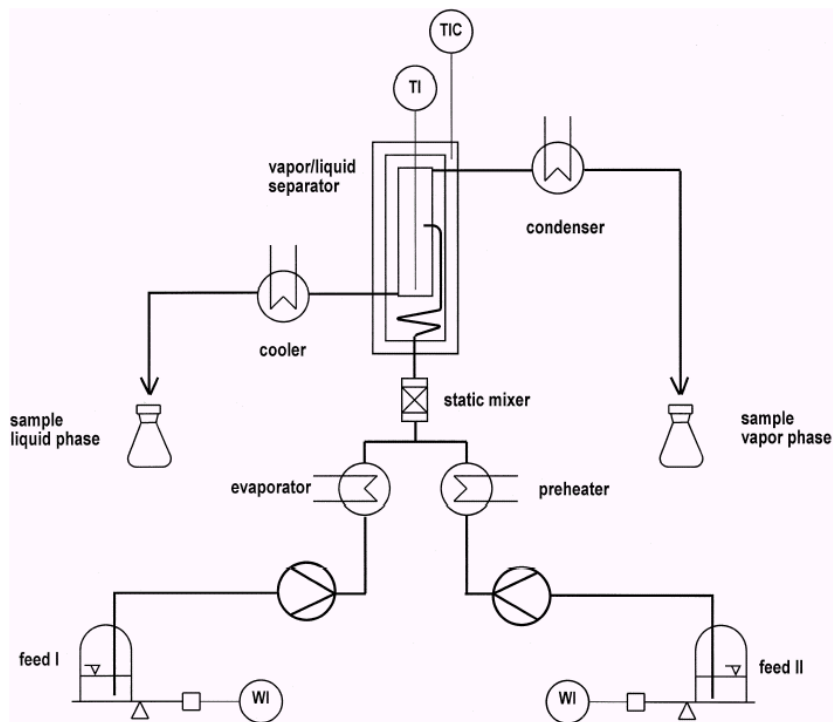


Fig. 1. Basic flowsheet of the Non-Recycle Flow Still (NFS).

Fig. 4.5: Experimental set-up by Reichl [28]

Another flow-type apparatus has been operated by Reichl et al. [28]. It was set up as a non-recycle flow still and, due to the short residence time, it was used to determine isobaric VLE data of thermally unstable components and of reactive mixtures (Fig.



4.5). Two esterification systems (methyl formate and ethyl acetate) and one etherification system (tert-amyl methyl ether) were investigated.

### Extrapolation methods

Patel [25] used a modified adiabatic calorimeter for the system Ethylene Oxide and Nonyl Phenol (Fig. 4.6). The measurements were carried out at temperatures of about 463 K. During the reaction the pressure was continuously measured. A linear extrapolation was used to obtain the binary VLE data. Best regression results were obtained with a Wilson model for the liquid phase and a modified RKS model for the gaseous phase.

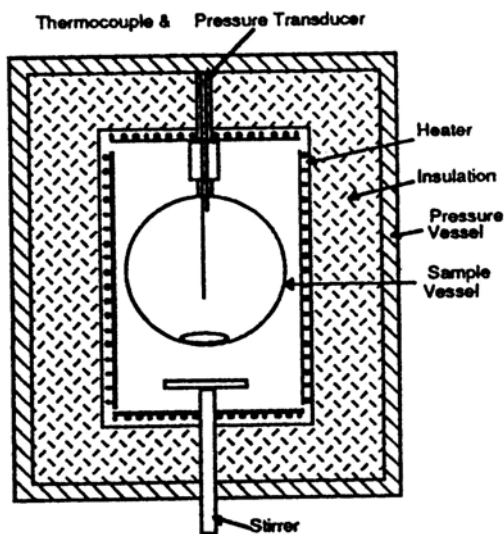


Figure 5. Automatic Pressure Tracking Adiabatic Calorimeter

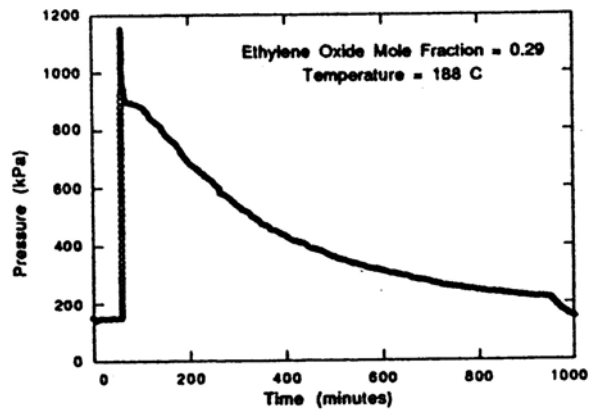


Figure 6. Ethylene Oxide/Nonylphenol Mixture Vapor Pressure vs. Time

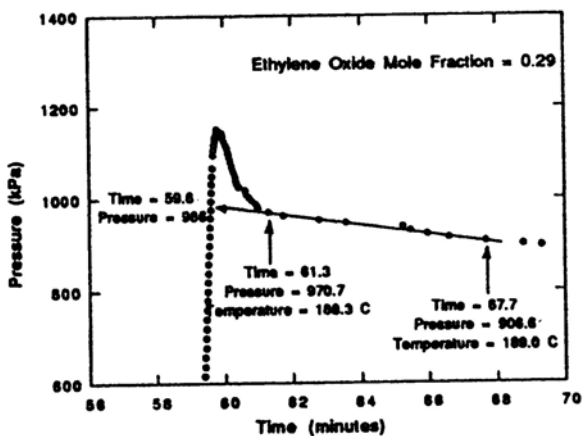


Figure 7. Pressure Correction to Compensate for Reaction

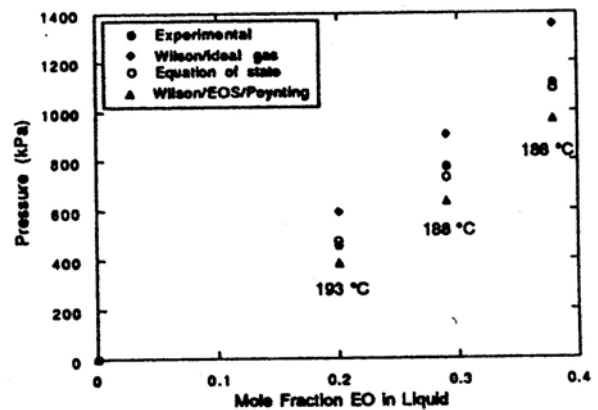


Figure 8. Experimental Data and Model Predictions. Ethylene Oxide + Nonylphenol system close to 190°C

Fig. 4.6: Experimental set-up by Patel [25]

The work of Patel inspired Arlt [2] to use a static apparatus in the same manner. The experiments were carried out in a 550 cm<sup>3</sup> static equilibrium cell which is located in a thermostatic oil bath at a given temperature with an accuracy of  $\pm 0.1$  K. The set up was modified to measure faster reaction velocities (down to a half-time of 15 min) by Tischmeyer [37] [38]. Stainless steel 1.4435, Teflon and glass were used for construction (Fig. 4.7).

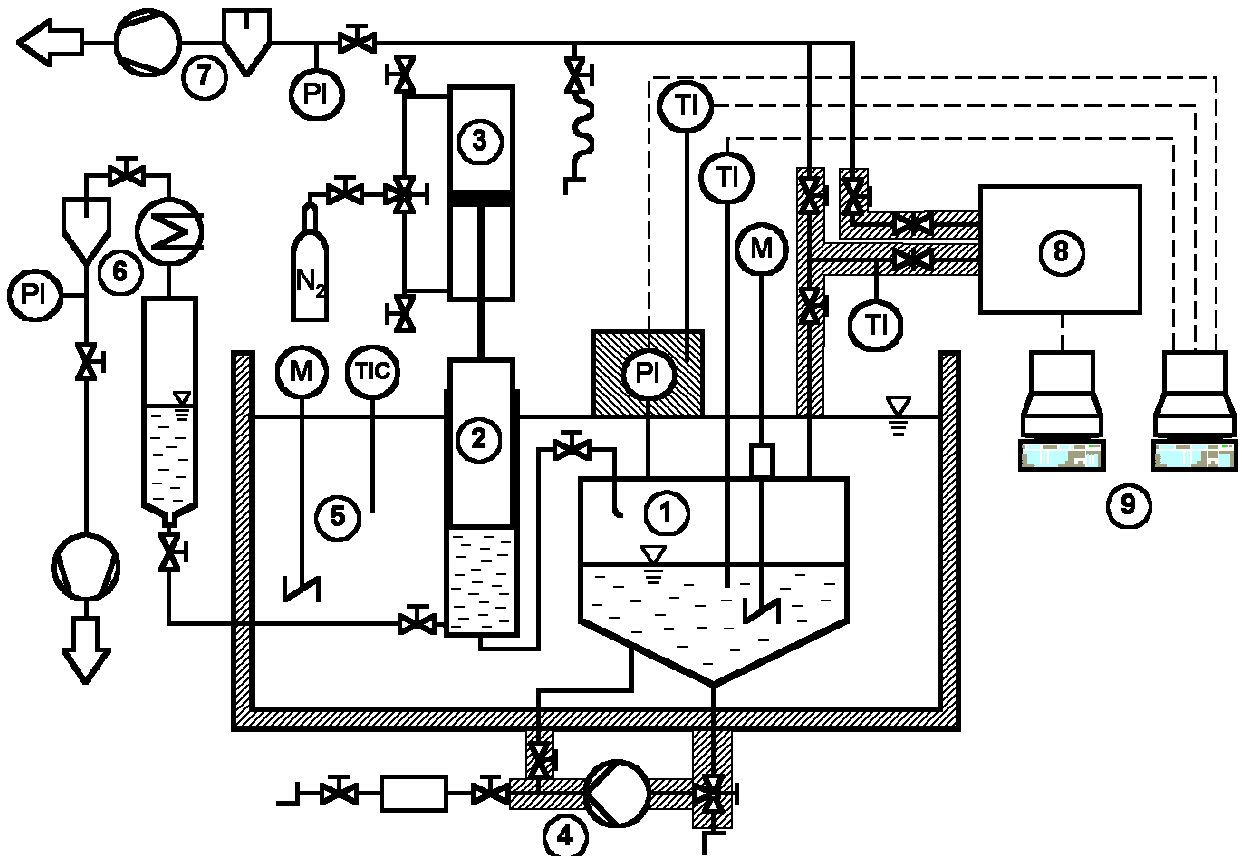
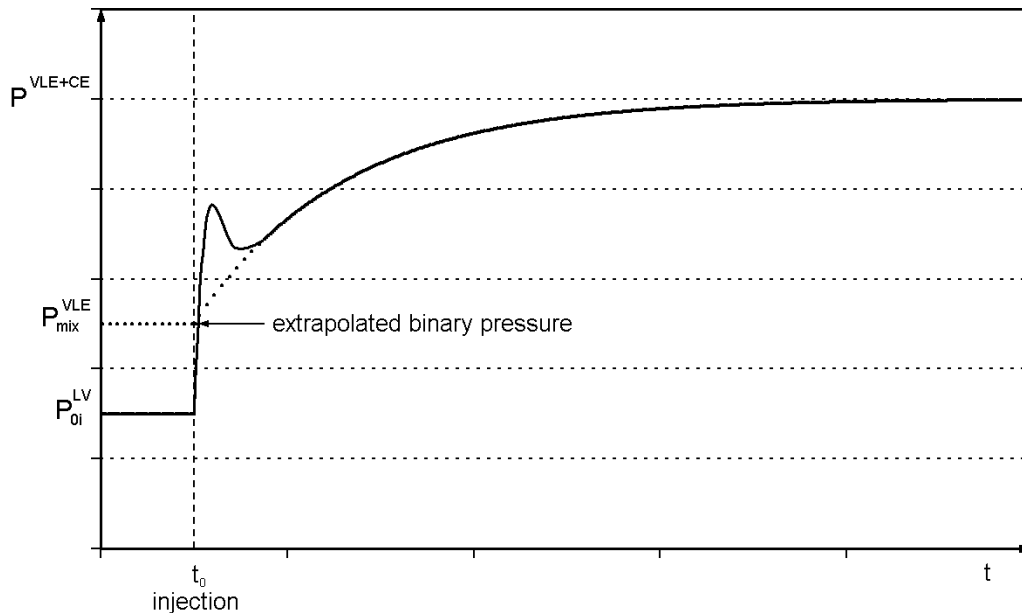


Fig. 4.7: Experimental set-up by Arlt [2] and Tischmeyer [37] [38]

The experiments are made as follows: the cell (1) is completely evacuated, the first compound is fed in and the pressure probe shows the vapour pressure. The second component is also degassed and loaded into an injection pump (2). Phase equilibrium is reached by mixing the two phases intensively using a stirrer head with magnetic coupling. The average mixing time is some seconds.

At the time  $t_0$ , the predefined amount of second compound is injected into the cell within less than 2 seconds. The precision of the injection is controlled by a linear transducer with an accuracy of  $\pm 10 \mu\text{m}$  which is calibrated to determine the injected mass at a given temperature. During the ongoing reaction, pressure and temperature are monitored continuously. If the total pressure of the binary mixture is lower than the total pressure at reaction equilibrium  $P^{\text{VLE+CE}}$ , the pressure over time diagram Fig. 4.8. holds. With the addition of a second component, the equilibrium is disturbed due to the heat of mixing and heat of reaction, it still takes some time to re-establish equilibrium conditions. Hence the first minutes after injection cannot be used to determine

the total pressure. After the temperature is equilibrated, a polynomial is fitted to pressure data and extrapolated to the time of mixing  $t_0$ . This approach was checked with non-reacting mixtures like acetic acid + water and methanol + water.



*Fig. 4.8: total pressure over reaction time*

The experimental result of the curve in Fig. 4.8 is one point  $P, T, x$ . Different polynomial approaches were examined for the extrapolation to  $t_0$ . The results for the corresponding binary pressure differ only within 0.06 kPa, which is about the accuracy of the pressure probe. If the reaction is very fast (half time less 15 minutes) then the heat of reaction influences the curve in Fig. 4.8 and the extrapolation is no longer possible. In this case, the authors take liquid samples and determine the interaction parameters of a  $G^E$ -model from this multicomponent data [38]. The same samples are used to determine kinetic data.

## Conclusions

The real behaviour of reacting systems cannot be measured directly. But fast on-line analysis (Roederer) or extrapolation methods (Patel, Arlt/Tischmeyer) allow to come very close. The method by Arlt/Tischmeyer is quite time consuming because the static cell has to be completely refilled for another point. The flow apparatus are very limited in the half time of the reaction, need a complex control and are quite expensive. But once the apparatus is working in equilibrium, the precision is quite good.

## METHODS FOR PREDICTING SEPARATION FACTORS

As always, the thermodynamics determines the basis of the separation. So, the first step is to evaluate the separation factors for the mixture to be separated.

### Algorithms

The first algorithm to predict separation factors for extractive distillation has been proposed in this conference (held in 1979) by Kolbe [21]. At that time, the Dortmund Databank has been initiated by Onken and established by Gmehling to correlate parameters of structure interpolating methods like ASOG and UNIFAC. As a test system, she used Cyclohexane-Benzene. First, she discovered functional groups that increase the separation factor. Second, she proposed molecules with two influential functional groups. Because a powerful tool to propose valid structures for molecules was not available, she pre-defined the carbon structure.

This first simple approach has been modified e.g. by van Dyk [10] using so-called genetic algorithms on the basis of the UNIFAC-method. They calculate the separation factors of 5 binary systems at equimolar ratio without and with the extractive solvent (ratio solvent to feed = 4:1). They find new solvents and compare them to the published ones.

This cannot be the complete assessment of the problem. As a rule, an extractive solvent influences most at the point of the azeotrope while often smaller separation factors can be found in the other parts of the equilibrium curve (see chapter 3.2). Further, other important questions like availability, corrosion, thermal decomposition and price are not included in the assessment. To conclude, the basic problem of searching an extractive solvent is not yet solved.

Van Dyk et al. [10] are missing binary interaction parameters in many cases, so a combination using predictive methods like COSMO-RS (see chapter 5.3) is the next step of the development.

### Structure interpolating methods

Many of the so-called predictive methods are really not. They determine parameters from existing experimental data and provide some kind of inter- and extrapolation of these data. Because of the existing large databanks like the Dortmund Data Bank, these methods have achieved a very high standard and are a most valuable tool for "predicting" (better: inter- or extrapolating) missing data. However, these methods look somehow into the past, since new classes of solvents and their behaviour cannot be predicted (compare with chapter 3.2). As stated above, van Dyk [10] assigned a penalty function to his algorithm, whenever group contribution parameters were missing.

### UNIFAC

UNIFAC has been developed by Fredenslund [12] on the basis of the UNIQUAC  $G^E$ -model. Because a large databank was available at Dortmund, a cooperate research program developed producing many updates of the method. Later, the groups divided, so the latest developments are splitted into modified UNIFAC Dortmund and modified UNIFAC Lyngby. The latest edition of the follow-up papers is Gmehling [13]. In former times, separate tables for separate applications (VLE, LLE, ...) existed. With the introduction of mod.UNIFAC, the complete thermodynamical data is incorporated in one parameter table for the sake of empirical temperature dependent functions for the parameters.

Tab 5.1: Latest UNIFAC Parameters (taken from Gmehling [13])

Main group	Structural group	Subgroup
Monoalkylated formamides (No. 49)		No. 93 (x = 3) No. 94 (x = 2)
Dialkylated formamides (No. 39)		No. 72 (x = 3, y = 3) No. 73 (x = 2, y = 2)
Monoalkylated amides (No. 47)		No. 92 (x = 3) No. 100 (x = 2)
Dialkylated amides (No. 48)		No. 101 (x = 3, y = 3) No. 102 (x = 2, y = 3) No. 103 (x = 2, y = 2)
Cyclic amides (No. 62)		No. 125
Cyclic alkylated amides (No. 46)		No. 86 (x = 3) No. 87 (x = 2) No. 88 (x = 1) No. 89 (x = 0)

Table 5.1 and Fig. 5.1 show the recent achievements. It is obvious that non-carbon neighbour groups cannot be represented by single functional groups but greater ensembles of functional groups have to be included in order to define UNIFAC-groups.

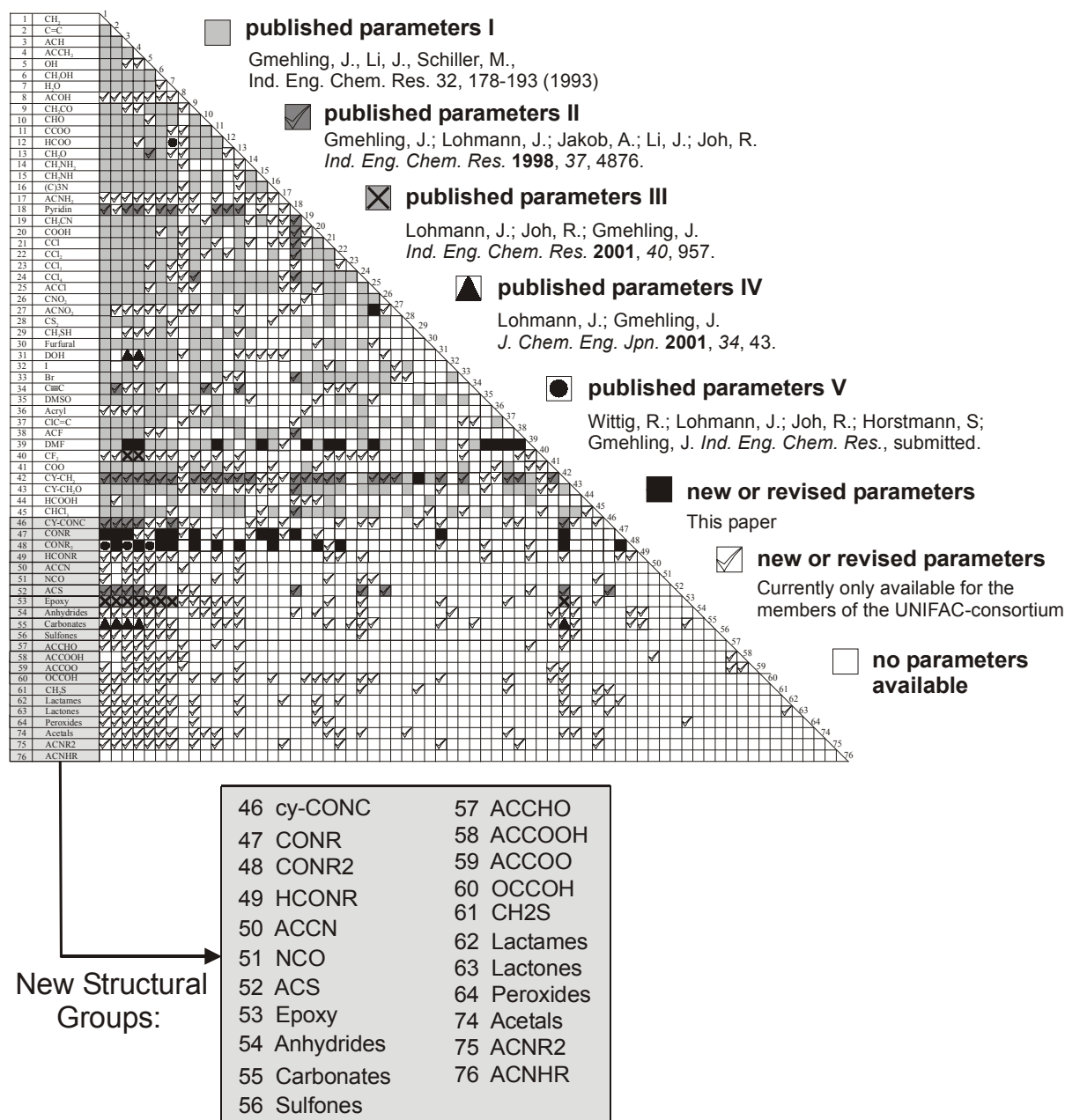


Fig. 5.1: Latest development of UNIFAC (Gmehling, 2001)

Fig. 5.1 gives an overview on the achievements of the method taken from Gmehling [13]. The group contributions for all the combinations of the 1<sup>st</sup> 40 groups are available due to the huge data bank, while the other 36 groups show big gaps. Here extensive measurements are needed. Because of industrial funding, the complete

table is not yet accessible in the public but the authors claim it will be after a certain time.

### MOSCED

Another predictive method is MOSCED (modified separation of cohesive energy density) [36]. This method is the extension of the regular solution model by Hildebrand to polar and associating systems including a Flory-Huggins term for components of non-equal size. It is assumed that the cohesive energy density is a linear function of these additive forces. Depending on the nature of the component, up to 9 pure component parameters are defined. Aqueous systems are outside the scope of this method.

Castells [6] compared this method to UNIFAC (Dortmund version, parameter release 2 from 1993) and others. They studied 11 alkanes in 67 solvents. UNIFAC showed a mean deviation of 9,8% and MOSCED of 8,8%. The author claims that the MOSCED-model was not developed by a huge data bank as UNIFAC. Further, the application of the pure component MOSCED parameter might be wider while UNIFAC needs binary interaction parameters of groups.

### **A priori predictive methods**

"Already in the 1970's and 80's, quantum chemical methods were very successful in describing the structure and properties of organic and main-group inorganic molecules. The Hartree-Fock (HF) method and its simplified semi-empirical modifications became standard tools for a vivid rationalization of chemical processes.

The underlying molecular orbital (MO) picture was, and still is, the most important theoretical concept for the interpretation of reactivity and molecular properties.

Nevertheless, quantum chemical methods were not used extensively for industrial problems, although most of the industrial chemistry produces organic compounds. (...) With the improvement of both the methodology and the algorithms of density functional theory (DFT, Parr [24]) in the last two decades, the situation changed significantly. DFT appears to be less sensitive to near degeneracy of electronic states, and furthermore incorporates some effects of electron correlation." (Schäfer [31]).

The present applications are in the field of chemical reactions (pathways, reaction rates and effect of catalysts) and of thermodynamical data as discussed by Schäfer [31]. He concludes that the solvent effect remains an unresolved phenomena as discussed by Wolbach et al. [42]. The authors use the quantum method from Hartree-Fock and the DFT method to determine at least one of the 2 association parameters of the Wertheim theory within SAFT. The major drawback is that this approach results in molecular geometries that exist in pure vacuum. In the vicinity of other molecules in dense fluids (like liquids), the electron charges and the binding angles are different. The authors conclude: "This work shows the applicability of quantum-mechanically derived thermodynamic parameters of association in reducing the number of parameters necessary to describe the phase behavior of hydrogen-bonding fluids. By using the results of our quantum-mechanical calculations, we have been able to fit pure-component VLE data for a number of associating fluids using the SAFT model with a reduction in the number of freely-adjustable parameters and little or no loss of accuracy."

One way to treat solvent effects is the use of continuum solvation models (CSM). One of the most effective ones is the COSMO (Conductor-like Screening) model by Klamt [17]. It is a particularly effective type of continuum solvation models, which uses the density functional theory to calculate the geometry of solute molecules and its screening charge density on their surface. The screening charge density represents the electrostatic interaction potential of the molecule and enables the calculation of the chemical potential of each component using an statistical mechanics approach.

The extension of COSMO to real fluids is COSMO-RS (Klamt, [18] [20]). Instead of assuming the surrounding of the molecule in focus (solutes) as an electrical conductor, the RS-method separates the surface of the solute molecule into pieces of given area and compares the screening charges with those of a second molecule (the solvent), treated in the same manner. A liquid now is considered to be an ensemble of almost closely packed ideally screened molecules, and the interactions of the molecules are expressed as pair-wise interactions of the screening charges. This includes electrostatic interactions as well as hydrogen bonding. By this reduction of molecular interactions to surface contacts, the statistical thermodynamics is reduced to a simple set of equations, which are similar, but even somewhat more accurate, than the UNIQUAC type of equations which are used in UNIFAC.

The theory assumes, that ideal behaviour compares to a complete neutrality of the charges of both molecules. Every deviation from this (called "misfit" by the authors) leads to activity coefficients different from unity. Furthermore, the energy to transport a molecule into an electrical conductor is a measure for the vapour pressure. As a result, all kind of thermodynamical data can be calculated. The model even works for multi-component systems. This method treats preferred enthalpic, i.e. interaction effects.

The accuracy of COSMO-RS depends strongly on the quantum chemical method used. Furthermore, the method carries internal parameters because electrostatic interaction are taken into account, only. The following atom-based internal constants are inside the method:

**radius of the elements**

used for cavity construction  
about 17% larger than Bondi radii

**dispersion constants (one per element)**

vdW energy contributions expressed by element-specific parameters

**effective contact area**

determines the number of independent neighbors for a molecule

**electrostatic misfit energy coefficient**

"self"-energy of a single segment of a surface divided by the surface charge density

**hydrogen bonding constants  $c_{hb}$  and  $\sigma_{hb}$**

$\sigma_{hb}$  is some threshold for hydrogen bonding and  $c_{hb}$  the strength coefficient

**ring correction coefficient  $\omega$**

**coefficient  $\lambda$  for the combinatorial part of the chemical potential**

**transfer constant  $\eta$**

connects reference states in gas and solution



These constants have been determined once [19] and have been improved in several revisions since then. A large number of different applications has been reported. The authors of this article presently specially reconsider the parameterization under the aspects of distillation. In this context the following calculations were successfully performed:

- suitable entrainers for extractive rectification in the system Benzene/Cyclohexane (Clausen [7] [8])
- vapor-liquid equilibrium in Alcohol/Water-systems (Clausen [7] [8])
- liquid-liquid equilibrium of Butanol-Water (Clausen [7] [8])
- activity coefficient at infinite dilution of pure and halogenated Hydrocarbons in Fish-oil (Clausen [7])
- 1-Octanol/Water partition coefficient (same precision as  $K_{OW}$ -UNIFAC but much better range of application) (Clausen [7], Maaßen [23])

Among the wide range applications, two examples have been chosen:

Figure 5.2 shows the VLE of n-Hexane - n-Butanol-1. Experimental data are compared to predictions of mod.UNIFAC Dortmund (3<sup>rd</sup> revision) and COSMO-RS. In both cases, the vapour pressure is calculated by a vapour-pressure correlation. Both methods predict the data quite well. The most important data, the separation factor, is shown in Fig. 5.3.

With other systems, the experimental data based UNIFAC method shows better results. In the example n-Pentane -Acetone, more prominent differences occur (fig. 5.4).

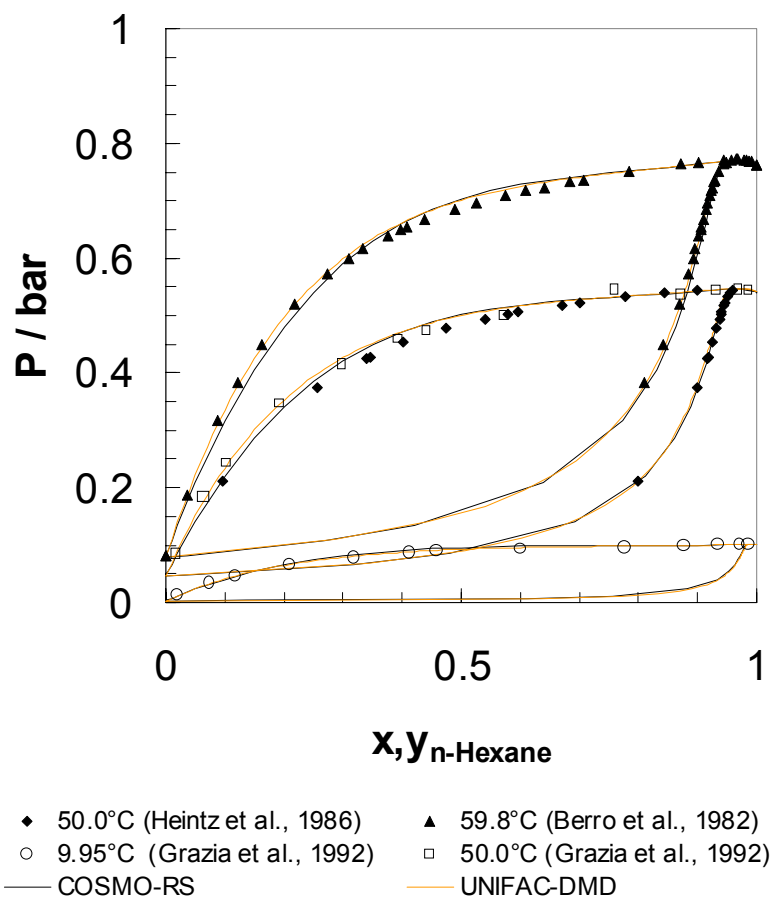


Fig. 5.2: Vapour-Liquid Equilibrium of n-Hexane - n-Butanol-1 @ 3 temperatures

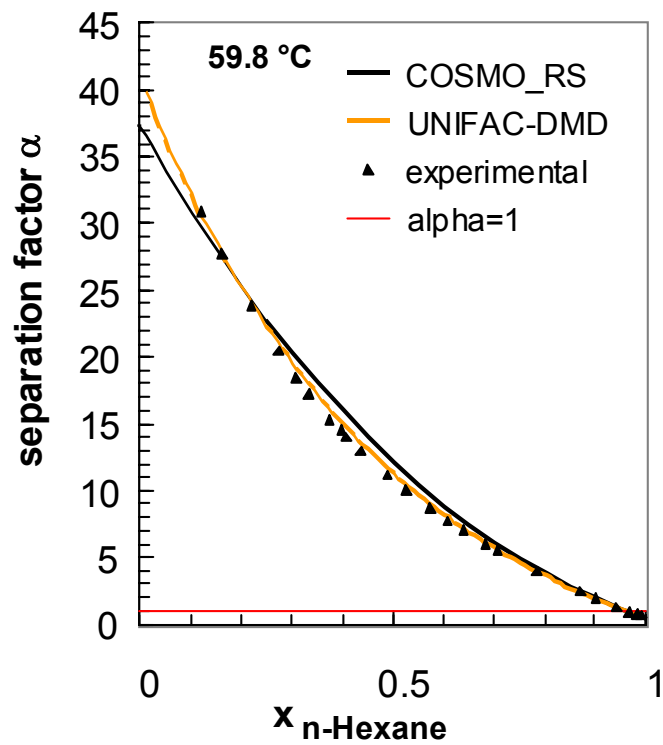


Fig. 5.3: Separation factor of the system *n*-Hexane-*n*-Butanol at 59,8°C

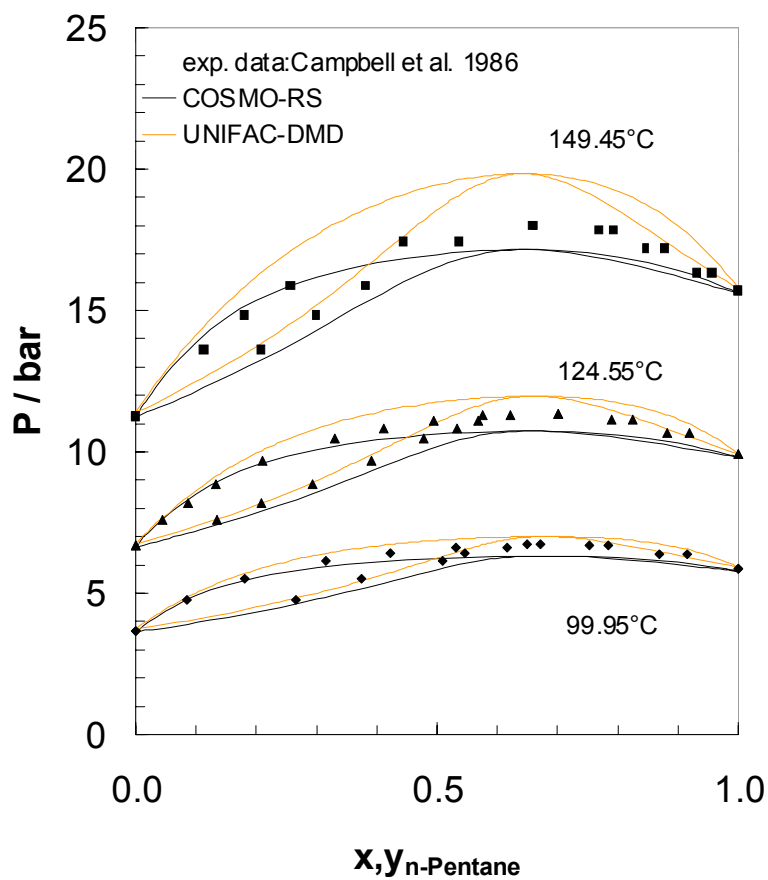


Fig. 5.4: Vapour-Liquid Equilibrium of *n*-Pentane -Acetone @ 3 temperatures

This is underlined by the plot of the separation factor in figure 5.5.

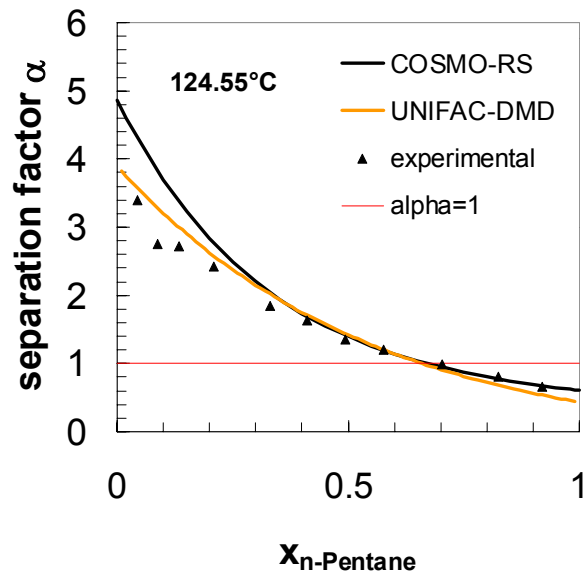


Fig. 5.5: Separation factor of the system *n*-Pentane-Acetone

In contrary to UNIFAC, COSMO-RS can resolve the differences between isomers. Figure 5.6 shows the near-ideal system isobutane-*n*-butane.

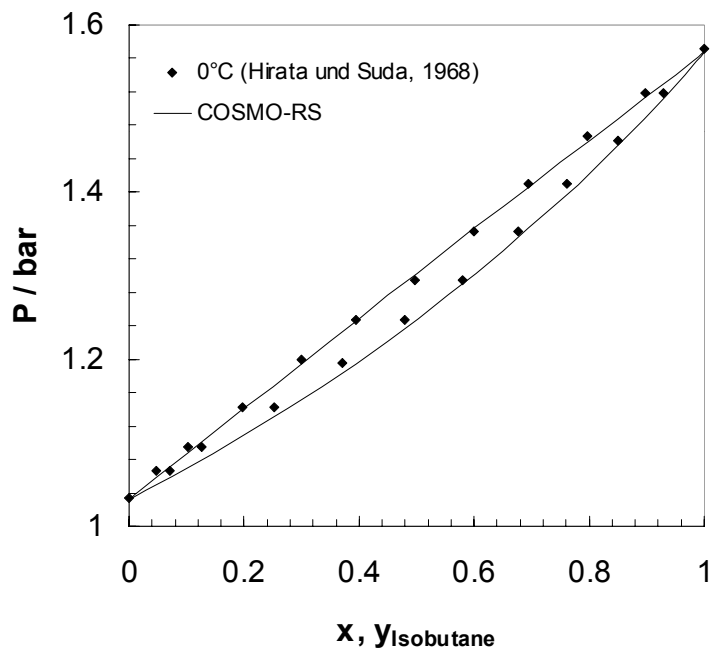


Fig. 5.6: Vapour-liquid equilibrium of iso Butane - *n*-Butane at 0°C

This fact is completely reproduced by COSMO-RS.

The application of COSMO-RS in distillation is in the early stages. One of the first contributions is by R.Taylor (Taylor [35]). It describes the extractive distillation of Acetone – Methanol by the aid of Water in a column of 34 stages and a reflux ratio of 4 at normal pressure. The column profiles are shown in figure 5.7. The  $G^E$ -model UNIQUAC with parameters determined from experimental data is compared to the prediction of COSMO-RS. The composition profile is very close and will be sufficient for the design of the separation equipment.

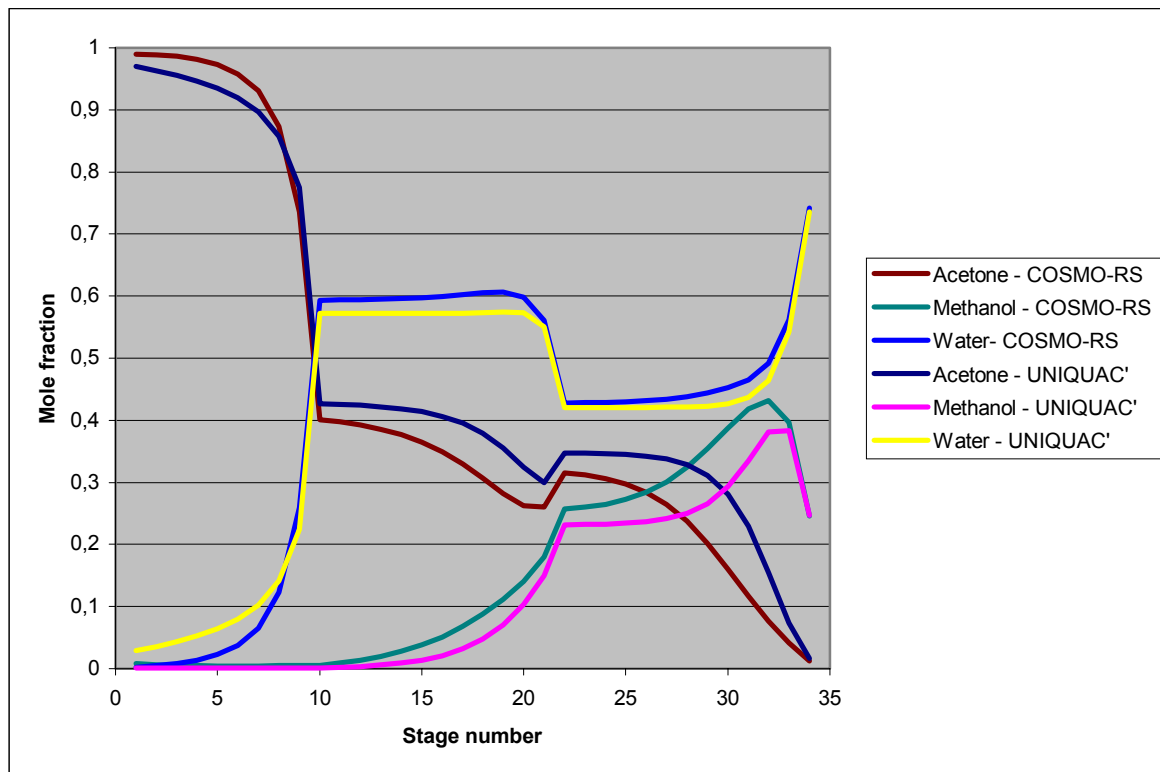


Figure 5.7: composition profiles in the extractive distillation of an acetone - methanol - water system predicted by COSMO-RS and UNIQUAC models.

### Equations of state

While in former times equations of state (EOS) based on empirical or semi-empirical extensions of the virial equation of state or on cubic equations of state, were used preferably in the gas industry, modern EOS are based on the so-called perturbation theory. If association is included by an expression by Wertheim [41] and dispersive forces are related to chains, one gets the so-called PC-SAFT EOS (perturbed-chain statistical association fluid theory) (Gross [14] [15]). Using conventional one-fluid mixing rules, the equation of state is applicable to mixtures of small spherical molecules like gases, non-spherical solvents, and chain-like polymers. Per pure component or homo-polymer, three pure component parameters have to be fitted to pure component thermodynamical data like vapour pressures and/or liquid densities. In addition, for associating fluids two more pure component parameters are needed.

The mixtures are described by a single binary interaction parameter which is constant for different pressures and temperatures, and molar weights. This EOS shows similar or even better results compared to  $G^E$ -models and other equations of state. Figure 5.8. shows results obtained by using the PC-Saft EOS in comparison to the original SAFT-EOS and experimental data.

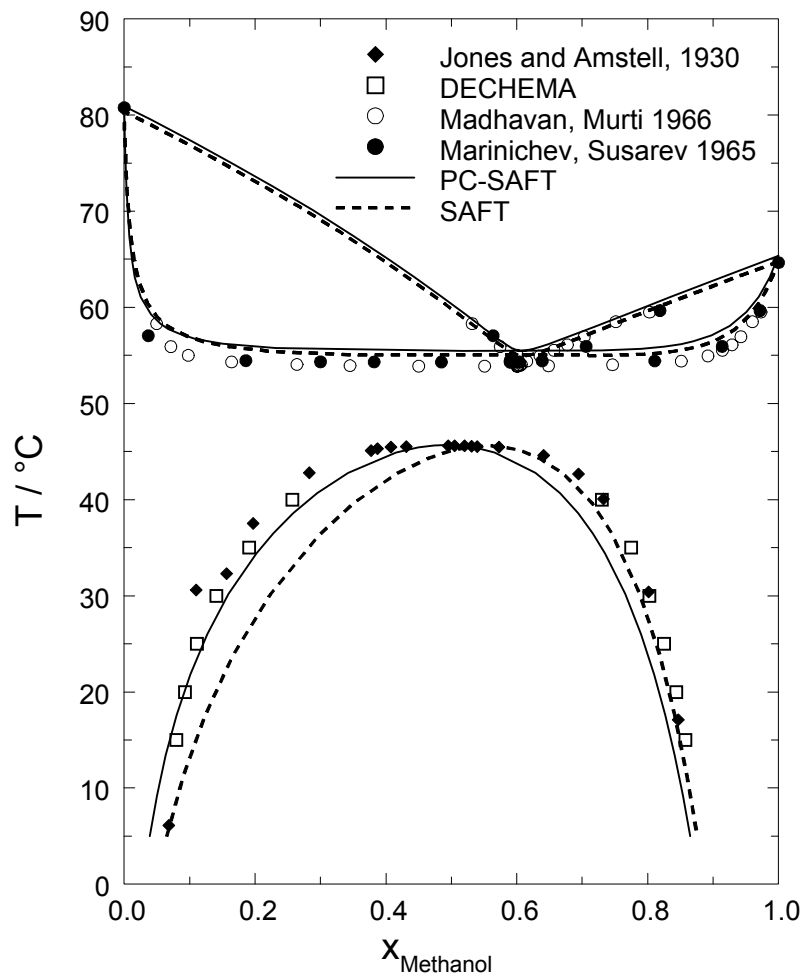


Fig. 5.8: Isobaric Vapour-Liquid Equilibrium and Liquid-Liquid Equilibrium for the system Methanol-Cyclohexane (taken from Gross, 2001a) experimental data by Jones, D.C., Amstell, S., J. Chem. Soc. 1930, 1316; Madhavan, S., Murti, P.S., Chem. Eng. Sci. 21, 1966, 465; and Marinichev, A.N.; Susarev, M.P., Zh. Prikl. Khim. 38, 1965, 1619  
lines: calculation by PC-SAFT ( $k_{ij}=0.051$ ) and SAFT [16] ( $k_{ij}=0.044$ )

This result is better than with any  $G^E$ -model based on one parameter set. It is surprising that engineers still stick to these models.

A wide spread cubic EOS is the PR-EOS [27]. It contains two pure component parameters which again are fitted to experimental data including critical data. One fluid mixing rules apply for the binary mixtures, leading to a  $k_{ij}$  for the energy term. It is obvious that a predictive  $G^E$ -model might be used to determine this parameter. Fig. 5.9 shows the result for the system Benzene-Propane. With the aid of COSMO-RS the prediction of the binary phase equilibrium is very close to the experimental points.

In this case mixture data has been generated by COSMO-RS. The  $k_{12}$  parameter of the PR-EOS was fitted to these data.

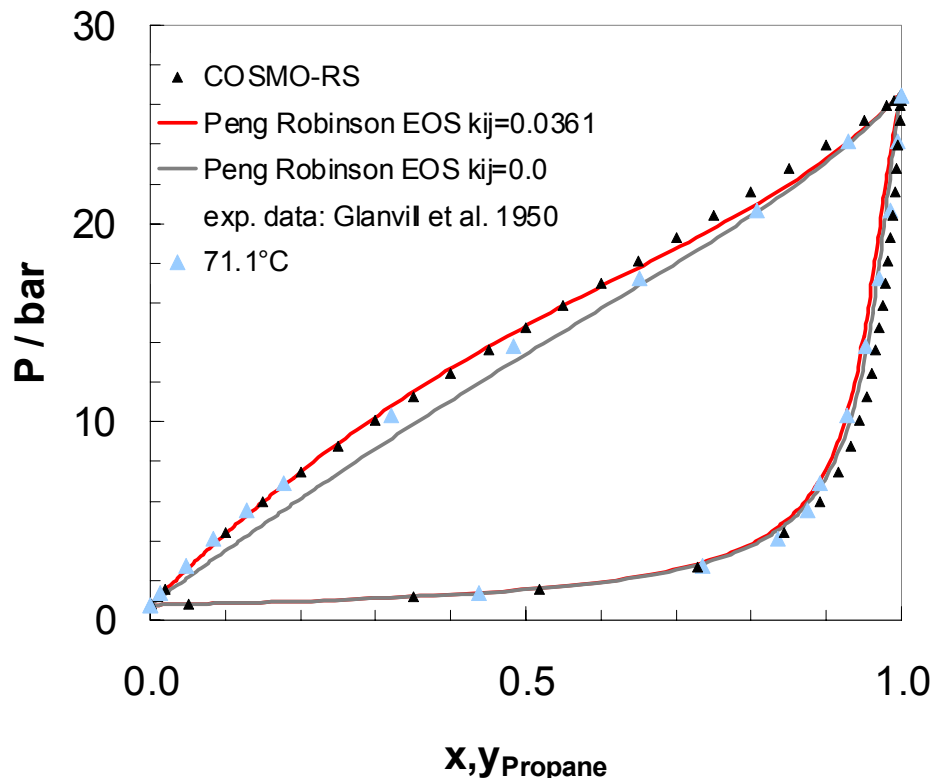


Fig. 5.9: VLE of Propane-Benzene at 71,1°C

exp. data (blue triangles) by J. W. Glanville, B. H. Sage, W. N. Lacey, Volumetric and phase behavior of propane-benzene system, *Ind. Eng. Chem.*, 42 (1950), 508-13; black triangles are COSMO-RS predictions, lines by the PR-EOS:

- a) with pure component parameters determined from critical data and  $k_{ij}=0$  for the grey line and
- b)  $k_{ij}$  calculated by generated mixture data from COSMO-RS for the red line; vapour pressures by a vapour pressure equation

## Conclusions

Structure-interpolating methods and predictive methods are a valuable tool for the process engineer. The accuracy of the structure interpolating method UNIFAC is very high because of a huge databank used to determine its many parameters, but predictive methods like COSMO-RS are becoming a serious alternative, but are more or less in the state of infancy. The progress is mainly determined by the accuracy of quantum chemical calculations. As Franke [11] states, this method is a useful tool for the process engineer with the special fact, that because of its sound physical background makes a calculation reliable but less accurate than UNIFAC.

The future belongs to the quantum chemical methods.

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