

Group contribution methods—ideal tools for the synthesis and design of separation processes*

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Abstract: Even though the reactor can be considered as the heart of a chemical plant, the greatest part of the costs (investments, operating costs) is in most cases due to the separation step in which the compounds leaving the reactor are separated in such a way that the desired products are obtained with the required purity, side-products are removed and unconverted reactants recycled. Various thermal separation processes can be applied for the separation.

The computer supported synthesis and design of separation processes requires a reliable knowledge of the phase equilibrium behavior of the system to be separated. During the last years powerful thermodynamic models have been developed, which allow the calculation of the various phase equilibria (VLE, LLE, SLE, etc.) of multicomponent systems using only binary experimental data. Furthermore with the help of a comprehensive data bank (Dortmund Data Bank) reliable predictive group contribution methods (g^E -models, equations of state) with a large range of applicability have been developed. In this paper the current status and typical results of the group contribution methods modified UNIFAC and PSRK are presented. At the same time the potential of these group contribution methods for the synthesis and design of separation processes will be highlighted.

INTRODUCTION

In the separation step various thermal separation processes are applied for the separation of the components in the outlet stream (unconverted reactants, products, undesired side products) of the reactor. The basic principle of a multistage countercurrent separation process is shown in Fig. 1. With the help of a separating agent (energy, mass separating agent) the system to be separated is divided into two streams (phases) of different composition. Depending on the type of separating agent one can distinguish different separation processes such as distillation, extraction, crystallization, absorption, adsorption, membrane processes.

In the case of distillation (or crystallization) energy is used as separating agent and the composition difference between the liquid and the vapor (or solid) phase is utilized for the separation. In other separation processes (extraction, absorption, adsorption, membrane processes) a mass separating agent, such as a selective solvent, adsorbent or membrane is applied rather than energy, to get the 'second phase (stream)'.

When the different separation processes are compared, great advantages become apparent for distillation processes. One reason is that the energy used as separating agent can easily be removed at the top of the column. In the case of mass separating agents a regeneration (e.g. of the solvents or adsorption medium) is required. Furthermore, distillation allows a simple realization of a large number of stages because of the large density difference between the coexisting liquid (L) and vapor phase (V). The above

*Lecture presented at the 7th International Chemistry Conference in Africa & 34th Convention of the South African Chemical Institute, Durban, South Africa, 6–10 July 1998, pp. 919–1024.

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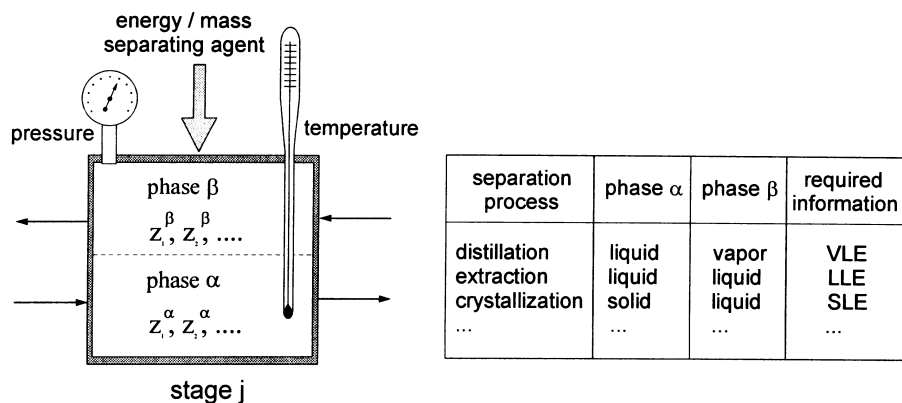


Fig. 1 Basic principle (one theoretical stage) of a countercurrent multistage separation process.

mentioned advantages are the main reasons for the application of distillation processes to 90% of the separation processes in the chemical industry. When the chemical and petrochemical industries as well as refineries and the gas processing industry are considered, the yearly throughput of distillation columns is about 5.2×10^9 t/year [1]. The main disadvantage is that distillation processes exhibit a high energy consumption. Thus in 1989 in the US around 3% of the total energy consumption was required to run about 40 000 distillation columns [2].

Depending on the phase equilibrium behavior and the number of components leaving the reactor the separation step can be quite complex. The different aspects which have to be considered are summarized in Fig. 2. During the development of the separation process the chemical engineer has to decide whether an alternative separation process, e.g. extraction, crystallization, absorption, adsorption, membrane process, supercritical extraction, etc. can compete with the baseline process (distillation). Furthermore he has to find out whether separation problems (azeotropic points, poor separation factors) need to be taken into account. In the case of separation problems, he has to figure out how these can be solved, e.g. with the help of a special distillation process, hybrid process, etc. For separation processes such as azeotropic or extractive distillation, extraction and absorption the chemical engineer has to select suitable solvents or solvent mixtures which show the necessary high selectivity and capacity. Then he has to decide how to arrange the selected separation processes. The number of possible separation sequences S_n dramatically increases with the increasing number of components n and separation processes T considered (for the equation for S_n see Fig. 2). However, this number can be reduced to the most economical one with the help of heuristic rules. Using the ideal stage concept the number of theoretical stages N_{th} can be calculated by solving the mass and energy balance (MESH equations) [3]. The objective of process synthesis is the development of the most economical solution for the given separation problem.

All these aspects which need to be considered require a reliable knowledge of the phase equilibrium behavior as a function of composition, temperature and pressure of the considered multicomponent system to be separated, including any subsystems involved. In accordance with Fig. 1 the typical question of the chemical engineer is: What is the composition of phase β and what is the pressure when phase β is in equilibrium with phase α of given composition and temperature?

Various sophisticated and reliable techniques have been developed for the experimental determination of the different phase equilibria. However, the measurement of phase equilibria for multicomponent systems is very time-consuming. For example the measurement of a 10 component system including all binary (45 systems), ternary (120 systems) and higher systems would require approximately 37 years of laboratory work, when the data are measured in 10 mole-% steps even when the data are taken only at one defined temperature (pressure) [3]. These numbers convince everyone that thermodynamic models which for example would allow the reliable prediction of the phase equilibrium behavior of multicomponent systems as function of composition, temperature and pressure using only binary experimental data would be most desirable.

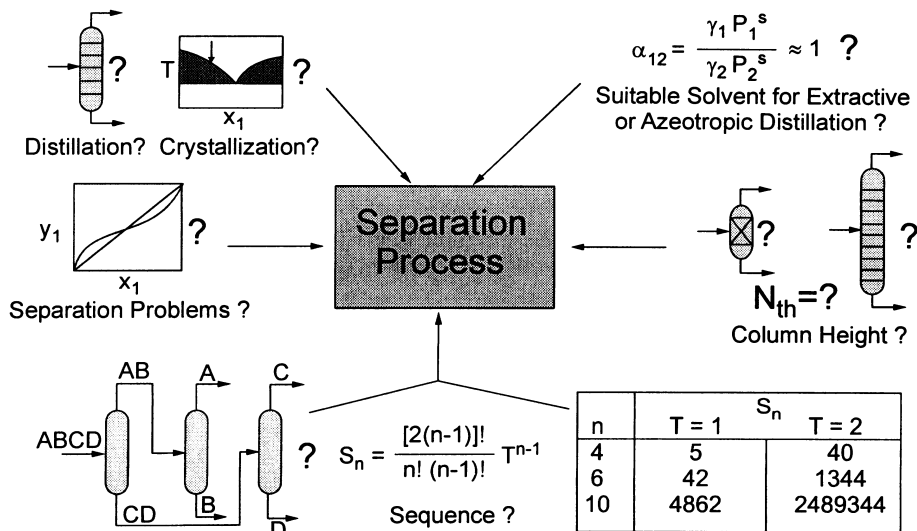


Fig. 2 Different aspects which have to be considered during the synthesis and design of separation processes.

Phase equilibrium thermodynamics

Starting from the isofugacity criterion two different relations can be derived to describe phase equilibria. In the case of VLE the following relations are obtained:

$$A : x_i \phi_i^L = y_i \phi_i^V \quad (1)$$

$$B : x_i \gamma_i P_i^S \approx y_i P \quad (2)$$

x_i (y_i) mole fraction of component i in the liquid (vapor) phase.

Using these relations two different expressions for the required distribution coefficients (K -factors) K_i and separation factors α_{ij} can be derived for VLE:

$$K_i = \frac{y_i}{x_i} = \frac{\phi_i^L}{\phi_i^V} \quad (3a)$$

$$K_i = \frac{y_i}{x_i} = \frac{\gamma_i P_i^S}{P} \quad (3b)$$

$$\alpha_{ij} = \frac{K_i}{K_j} = \frac{\phi_i^L \phi_j^V}{\phi_i^V \phi_j^L} \quad (4a)$$

$$\alpha_{ij} = \frac{K_i}{K_j} = \frac{\gamma_i P_i^S}{\gamma_j P_j^S} \quad (4b)$$

While in approach A the real behavior in the liquid and vapor phase is described with the help of fugacity coefficients ϕ_i , in approach B, activity coefficients γ_i (g^E -models) are used to account for the deviation from ideal behavior in the liquid phase. Additionally vapor pressures P_i^S are required in approach B. Similar simple relations can also be derived for LLE, SLE and so on [3].

Thermodynamic models

Approach A: equations of state

The required fugacity coefficients ϕ_i for the liquid (L) and the vapor (V) phase can be calculated with the help of an equation of state (EOS), which is able to describe the PVT-behavior of both fluid phases. The

first suitable equation to describe the PVT behavior of the liquid and the vapor phase and the observed condensation, vaporization and critical phenomena was the van der Waals equation of state published in 1873. In the van der Waals EOS a repulsive parameter b and an attractive parameter a are used to describe the PVT behavior including the two-phase region, whereby the two parameters can be obtained from critical data (e.g. critical pressure P_c and critical temperature T_c). For the application of equations of state to mixtures, reliable mixing and combination rules for both parameters are additionally required.

Today modifications of the cubic van der Waals equation of state such as the Soave-Redlich-Kwong (SRK) [4] or the Peng-Robinson (PR) [5] equation of state are used. In both equations a temperature dependence $\alpha(T)$ of the attractive parameter a_{ii} has been introduced using the acentric factor ω_i as additional information, to obtain a more reliable description of the pure component vapor pressure data. The equation of state approach shows different advantages when compared with g^E -models. However, the classical quadratic mixing rules used up to 1979 provided only poor results for systems containing polar compounds. This problem was solved with the help of so-called ' g^E -mixing rules' proposed by Huron & Vidal [6]. Huron & Vidal combined the successful and flexible g^E -models with the advantageous equation of state approach. In their approach the required attractive parameter $a(T)$ for a given composition z_i (mole fraction x_i resp. y_i) and temperature T can be obtained using the pure component parameters a_{ii} and b_i , the mixture parameter b ($b = \sum z_i b_i$) and the excess Gibbs energy g^E .

$$\frac{a(T)}{b} = \sum \frac{z_i a_{ii}(T)}{b_i} + \frac{g^E}{-0.6931} \quad (5)$$

This means that the different correlative local composition g^E -models can be directly applied to fit the required binary parameters and to apply these parameters to describe the phase equilibrium behavior of higher systems.

Approach B: g^E -models

The calculation of phase equilibria using approach B is much simpler. However, g^E -models are required which allow the prediction of phase equilibria for multicomponent systems using binary data alone. The breakthrough in the field of g^E -models was achieved by Wilson [7] who introduced the so called local composition concept. With this concept he succeeded in predicting the behavior of multicomponent systems using only binary data. Later, other local composition models such as NRTL [8] and UNIQUAC [9] were proposed. All three g^E -models are successfully used in the different process simulators.

Parameter fitting

Both approaches allow the calculation of phase equilibria for multicomponent systems using only binary experimental data. A precondition for the correct description of phase equilibria of multicomponent systems is the determination of reliable binary interaction parameters. Apart from phase equilibrium data, excess properties can be used for fitting these parameters. In chemical industry often only VLE data are used for fitting the parameters. However, it is recommended to fit the required interaction parameters simultaneously to all available reliable experimental data (VLE, γ^∞ , h^E , ...) [10], since the parameters obtained by a simultaneous fit provide a more reliable description of the real behavior across the whole composition range and a large temperature range.

Today nearly all published experimental data for fitting the required binary parameters are available in computerized data banks, such as for example the Dortmund Data Bank (DDB). The DDB contains not only all phase equilibrium data and excess properties available world-wide but also all the experimental pure component data published. The number of data sets listed in Table 1 gives an idea of the amount of experimental data available world-wide.

Comparing the advantages and disadvantages of the different approaches, approach A has many advantages. In contrast to approach B the equation of state concept is not limited to subcritical systems. Furthermore equations of state allow not only the calculation of phase equilibria but also that of densities and all other thermodynamic properties, such as enthalpies (e.g. heats of vaporization), entropies, etc. For the design all these properties are required as additional information when approach B is used.

Table 1 Current status of the Dortmund Data Bank (May 1998)

Data bank	Number of data sets	References
VLE of normal boiling substances	18 000	4400
VLE of low boiling substances	16 000	2100
VLE of electrolyte systems	1900	210
Liquid–liquid equilibria	10 700	1650
Heats of mixing	13 600	2200
Activity coefficients at infinite dilution	34 400 values	500
Gas solubilities	8600	1000
Excess heat capacities	1050	225
Azeotropic data	42 000 values	5550
Solid–liquid equilibria	7300	1250
Excess volumes	12 000	1800
Adsorption equilibria	3050	380
Pure component properties (under construction)	83 000	12 600

Group contribution methods

Since the application of g^E -models and equations of state is limited to systems for which experimental data for all binary systems are available, attempts to develop predictive models has been continuing for more than 100 years. Very reliable predictive models with a large range of applicability have been developed in the last 25 years using the group contribution concept. In group contribution methods it is assumed that the mixture does not consist of molecules but of functional groups. The great advantage of the ‘solution of groups’ concept is that the number of functional groups is much smaller than the number of possible compounds. VLE data from the Dortmund Data Bank have mainly been used for fitting the required group interaction parameters for the group contribution methods ASOG [11] and UNIFAC [12,13].

Although the original UNIFAC method [12,13] is used world-wide for the prediction of VLE, it shows some weaknesses. For example, only poor results are obtained for activity coefficients at infinite dilution (γ^∞) including the temperature dependence and also for systems with compounds very different in size. This is not surprising, since with the database used (mainly VLE data) for fitting the group interaction parameters only a limited concentration range (5–95%) is covered, compounds of similar size are considered and no quantitative information about the temperature dependence is available.

A modified UNIFAC method [14] has been developed to eliminate most of the above-mentioned weaknesses. In the modified UNIFAC method the combinatorial part has been slightly changed, new main groups have been defined and the temperature dependent parameters introduced are fitted simultaneously to the different thermodynamic properties (VLE, LLE, heats of mixing, SLE data of eutectic systems, γ^∞ , azeotropic data). This means that the whole composition range as well as a large temperature range is covered and (with heats of mixing data) quantitative information on the temperature dependence is used. Figure 3 shows typical VLE results obtained for alcohol–alkane systems using the modified UNIFAC method. The behavior of all systems is predicted with the same group interaction parameters for the alcohol–alkane group. It can be seen that the predicted results are in good agreement with the experimental data and that also the azeotropic points are predicted within ± 1 mole-%.

Today modified UNIFAC contains around 60 functional groups [15]. Because of the importance of the modified UNIFAC method for process simulation, a continuous revision and extension takes place within a company consortium.

Group contribution equation of state

The group contribution concept can be directly applied in the so-called g^E -mixing rules for equations of state. This lead to a predictive group contribution equation of state. In the PSRK (Predictive SRK)-model

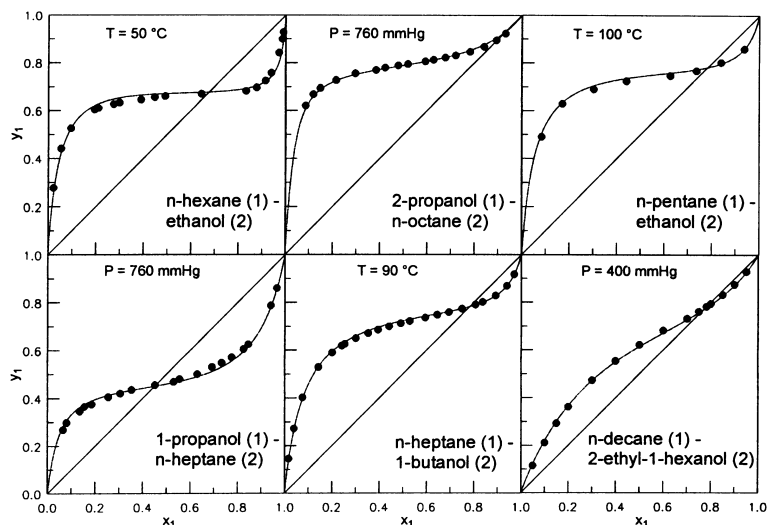


Fig. 3 VLE results of the modified UNIFAC method for different binary alcohol-alkane systems.

[16] the Soave-Redlich-Kwong (SRK) equation of state is combined with the group contribution method UNIFAC to get the required attractive parameter $a(T)$ for the given mole fraction z_i (x_i for the liquid and y_i for the vapor phase) from the predicted g^E -values ($g^E = RT \sum x_i \ln \gamma_i$)

$$\frac{a(T)}{b} = \sum \frac{z_i a_{ij}(T)}{b_i} + \frac{g^E + RT \sum z_i \ln(b/b_i)}{-0.64663} \quad (6)$$

In the PSRK model the existing parameters of the UNIFAC method (Hansen *et al.* [13]) are used to calculate the required g^E -values. To extend the range of applicability of the PSRK method the main groups for 19 gases were added to the existing parameter table (Fischer & Gmehling [17], Gmehling *et al.* [18]), whereby a large part of the required group interaction parameters have been fitted using gas solubility and VLE data for low boiling substances stored in the Dortmund Data Bank (see Table 1). Figure 4 shows typical VLE results of the PSRK model for H_2S -alkane systems. It can be seen that the group contribution concept can also successfully applied for supercritical compounds, thus making possible the synthesis and design of all separation processes where supercritical compounds are present, e.g. absorption, supercritical fluid extraction, etc.

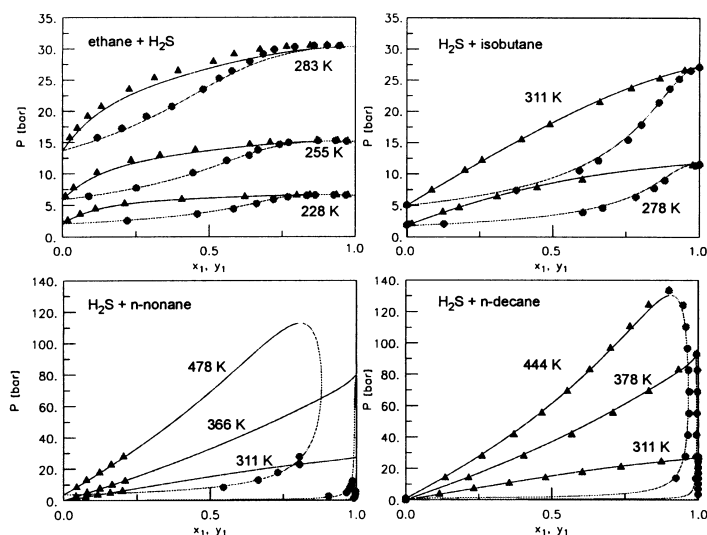


Fig. 4 Experimental and predicted PSRK VLE results for different H_2S -alkane-systems.

Applications

The knowledge of the real behavior of fluid mixtures does not only allow the calculation of the different phase equilibria or excess properties. Reliable thermodynamic models are of particular importance for the synthesis and design of separation processes. Furthermore the reliable knowledge of the real behavior (γ_i , φ_i) of fluid mixtures is also required for solving other problems of industrial interest. Important applications include the calculation of chemical equilibria, the derivation of standard thermodynamic properties from reaction enthalpies and equilibrium compositions and the consistent simultaneous description of reaction rates, chemical equilibria and phase equilibria required for example for reactive separation processes such as reactive distillation (extraction) or chemical absorption. With the help of reliable activity coefficients or fugacity coefficients the flash points of flammable liquid mixtures or the fate of a chemical compound in the environment can be estimated. The knowledge of the real behavior is also required for the description of diffusional transport processes using more sophisticated potentials. Thermodynamic models are also helpful for the selection of suitable working fluids (e.g. alternative refrigerants) or to judge the suitability of solvents such as CO₂ for chemical reactions.

Group contribution methods: Ideal tools for the synthesis and design of separation processes

During the synthesis and design of separation processes different aspects have to be considered (see Fig. 2). For all such aspects a reliable knowledge of the phase equilibrium behavior is required, so that the predictive models referred to above are ideal tools for this kind of work. This will be demonstrated for distillation processes. Ordinary distillation cannot be applied when the system to be separated shows azeotropic behavior. Since distillation processes show various advantages when compared with other separation techniques it is the task of the chemical engineer to consider special distillation processes. In Fig. 5 the condition for azeotropic behavior is given for binary systems showing a positive deviation from Raoult's law. At the azeotropic point the separation factor α_{12} is equal to unity for homogeneous systems. From this information a simple relation can be derived which is given in Fig. 5. Using this relation the occurrence and disappearance of azeotropic behavior can be predicted as function of temperature when only the activity coefficients at infinite dilution γ_i^∞ and the ratio of the vapor pressures are known, the temperature dependencies of these properties being described by the Clausius–Clapeyron and the Gibbs–Helmholtz equation [3].

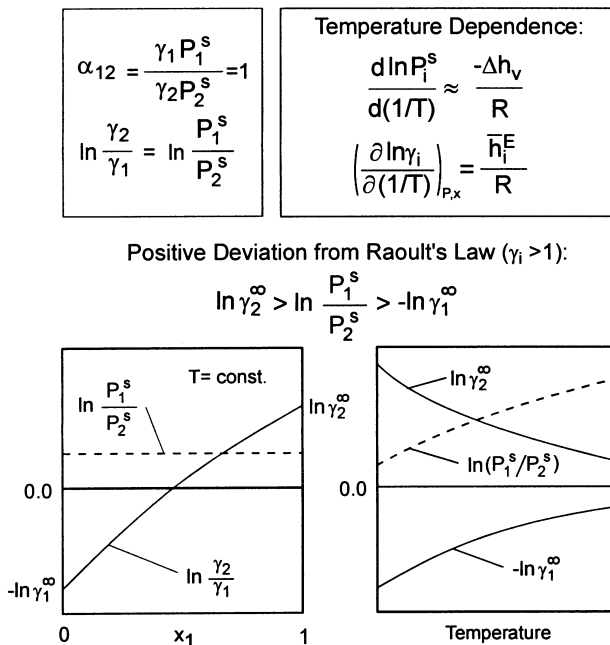


Fig. 5 Conditions for the occurrence of azeotropic points in homogeneous binary systems with positive deviation from Raoult's law.

As can be seen from Fig. 5, azeotropic points mainly occur when the vapor pressures of the considered components are similar or when the binary system considered shows strong real behavior. Azeotropic behavior can also occur in ternary and quaternary systems. The azeotropic points in ternary and quaternary systems can also be estimated with the help of the group contribution methods introduced. In homogeneous systems the program only has to find the composition for which all separation factors α_{ij} are equal to unity. This means that it can easily be checked with the help of group contribution methods whether the multicomponent system to be separated shows separation problems (azeotropic points). In Table 2 a comparison of the experimental and the predicted azeotropic points is shown for a quaternary system. It can be seen that not only all observed azeotropic systems have been discovered using modified UNIFAC, at the same time the azeotropic composition is in good agreement with the experimental findings.

Table 2 Predicted (modified UNIFAC) and experimental azeotropic data for the quaternary system benzene(1)–cyclohexane(2)–acetone(3)–ethanol(4) and all its subsystems at atmospheric pressure

System	Predicted				Experimental*			
	Type of azeotrope	t (°C)	y _{1,az}	y _{2,az}	Type of azeotrope	t (°C)	y _{1,az}	y _{2,az}
1-2	homPmax	77.5	0.543		homPmax	77.6	0.543	
1-3	none				none			
1-4	homPmax	68.0	0.537		homPmax	67.9	0.552	
2-3	homPmax	54.3		0.221	homPmax	53.2		0.248
2-4	homPmax	65.3		0.545	homPmax	64.8		0.553
3-4	none				none			
1-2-3	none				none			
1-2-4	homPmax	65.1	0.126	0.441	homPmax	64.9	0.113	0.462
1-3-4	none				none			
2-3-4	none				none			
1-2-3-4	none				n.a.			

*Mean values of the experimental data stored in the Dortmund Data Bank.
n.a., not available.

Depending on the azeotropic behavior as function of temperature different distillation processes without the use of an entrainer can be applied. These distillation processes are summarized in Fig. 6. If the azeotropic behavior disappears at lower or higher pressures a separation is possible by vacuum or pressure distillation. Binary systems with a heterogeneous azeotropic point can be separated easily in two columns. Furthermore a strong pressure dependence of the azeotropic composition can be exploited to separate the azeotropic system in two columns working at different pressures (pressure swing distillation). A sophisticated software package in combination with a reliable thermodynamic model of course should be able to recognize all these interesting possibilities.

More important than the above mentioned distillation processes is the separation of azeotropic systems or systems with poor separation factors by azeotropic or extractive distillation. In these processes a suitable solvent is applied. Both separation processes are shown in Fig. 7. In the case of azeotropic distillation a solvent is required which forms a lower boiling azeotrope which can be obtained at the top of the column, whereby the new low boiling azeotrope should not cause any further separation problem. Therefore the formation of heterogeneous azeotropic points is preferred. Toluene can be applied as a suitable solvent for the separation of pyridine from water. The ternary diagram with the azeotropic points, binodal curve, boundary residual curves and the column configuration with the streams is also shown in Fig. 7. Selective high boiling solvents are required for extractive distillation. The task of the entrainer is to alter the separation factor, so that this value becomes very different from that without the entrainer. A suitable criterion for the selection of selective solvent is the selectivity at infinite dilution S_{12}^{∞} , i.e. the ratio of the activity coefficients at infinite dilution in the entrainer. In Fig. 7 the experimental and

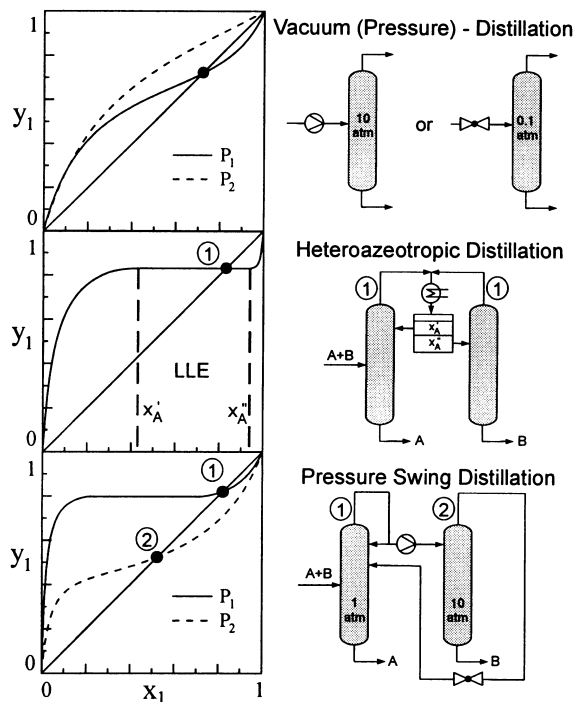


Fig. 6 Special distillation processes for the separation of azeotropic systems without the use of an entrainer.

predicted γ^∞ -values of benzene and cyclohexane are given as a function of temperature for the solvent aniline. It is obvious that aniline alters the ratio of the γ^∞ -values greatly, so that the separation factor becomes different from unity and the separation of the azeotropic system benzene + cyclohexane (used as an example for the separation of aliphatics from aromatics) can be performed by extractive distillation as shown in Fig. 7 together with the column configuration.

The selection of suitable solvents for azeotropic or extractive distillation requires only a reliable knowledge of the phase equilibrium behavior, in particular activity coefficients at infinite dilution and azeotropic data. These data can be predicted with the help of the modified UNIFAC method or called up from a comprehensive factual databank such as the Dortmund Data Bank. A sophisticated software

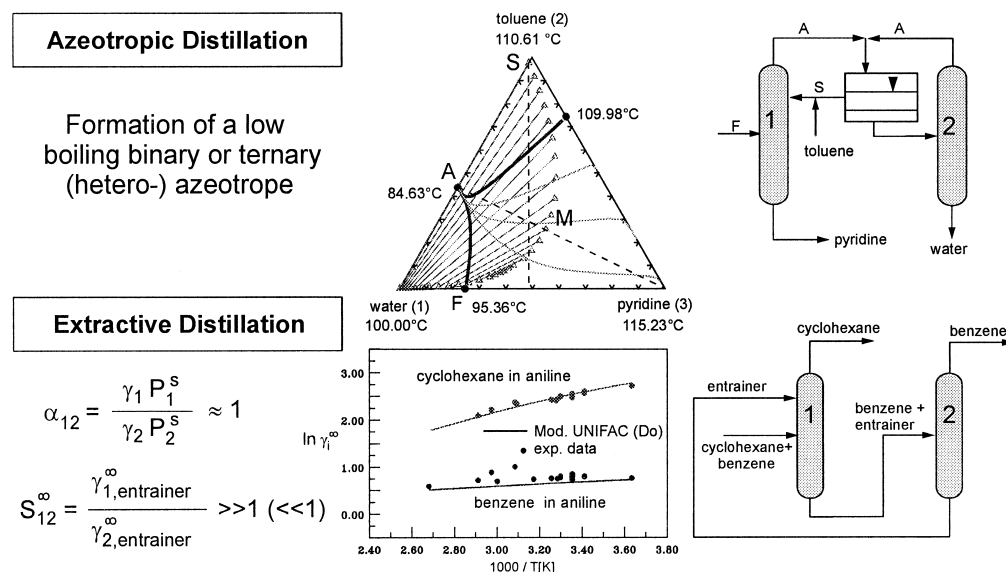


Fig. 7 Examples of the separation of azeotropic systems by azeotropic or extractive distillation.

package has been developed for the synthesis and design of separation processes. Besides the search for azeotropic points in multicomponent systems, the construction of residual curves or contour lines it allows the selection of suitable solvents with the help of thermodynamic models or the Dortmund Data Bank [19]. Using thermodynamic models all those compounds (at present 11 200 components) in the Dortmund Data Bank can be considered as potential solvents. Before the program starts with the search it will remind the user whether one of the alternative distillation processes shown in Fig. 6 can be applied for the given system. In Table 3 an extract of the solvents selected for the dehydration of ethanol by extractive and azeotropic distillation is listed.

Table 3 Suitable solvents (extract) for the separation of ethanol from water by extractive and azeotropic distillation

Components to be separated:

(1) Ethanol	C ₂ H ₆ O	64-17-5
(2) Water	H ₂ O	7732-18-5

System pressure = 101.325 kPa

Tb(1) = 351.43 K

Tb(2) = 373.15 K

Azeotropic data for system (1)–(2):

Type of azeotrope: homPmax Tb = 351.30 K

Model: modified UNIFAC (Dortmund)

List of solvents introducing no further azeotrope (extractive distillation entrainer)

Selective solvent (3)	Tb K	alpha(1,2), inf.	Types of azeotropes introduced: Tm(3) K			
			(1) – (3)	(2) – (3)	(1) – (2) – (3)	
1,2-Ethanediol	470.62	2.945 (398.40 K)	none	none	none	261.65
Dimethyl sulfoxide	466.74	4.308 (397.10 K)	none	none	none	291.69
N-methyl-2-pyrrolidone	475.13	0.424 (399.90 K)	none	none	none	248.75
Epsilon-caprolactone	542.78	0.621 (422.45 K)	none	none	none	271.85
N-methyl-2-piperidone	483.42	0.409 (402.67 K)	none	none	none	n.a.
N-methyl-6-caprolactam	510.21	0.360 (411.59 K)	none	none	none	n.a.
N-octyl-2-pyrrolidone	603.84	0.325 (442.80 K)	none	none	none	253.15
3-dodecanol	486.32	0.612 (403.63 K)	none	none	none	n.a.

minimum boiling point difference (entrainer – binary mixture) = 40.00 K

minimum required value for alpha (1,2 or inverse) at infinite dilution = 1.500

List of solvents introducing a ternary heterogeneous azeotrope

Solvent (3)	Tb (az) K	yaz (1)	yaz (2)	yaz (3)	Tm (3) K
Benzene	337.91	0.2657	0.2070	0.5273	278.68
Toluene	347.24	0.4562	0.2842	0.2596	178.16
Cyclohexane	336.24	0.2938	0.1595	0.5467	279.75
Methylcyclohexane	343.67	0.4093	0.2248	0.3659	146.55
Hexane	330.19	0.2439	0.1203	0.6357	177.85
Pentane	306.77	0.0690	0.0396	0.8913	143.45
1,2-Dichloroethane	341.78	0.2527	0.2578	0.4896	237.65
Tetrachloromethane	335.50	0.2400	0.1819	0.5781	250.77
Diisopropyl ether	333.74	0.1887	0.1799	0.6314	186.35
Dipropyl ether	345.46	0.2992	0.3040	0.3967	147.05
Ethyl tert-butyl ether	337.77	0.1859	0.2223	0.5918	179.15
Ethyl acetate	344.27	0.0989	0.3096	0.5925	189.55
Isopropyl acetate	348.31	0.2500	0.3546	0.3954	199.75

CONCLUSION

The prerequisite for the synthesis, design and optimization of separation processes is the reliable knowledge of the phase equilibrium behavior of the system to be separated. Since the measurement of phase equilibria of multicomponent systems is very time-consuming, thermodynamic models are required. Sophisticated and powerful g^E -models and equations of state with improved mixing rules have been developed. If binary data are not available reliable group contribution methods (g^E -models, equations of state) can be applied. These predictive models are ideal tools for the synthesis and design of separation processes. Therefore these methods have been integrated into sophisticated software packages. In the future the application of these programs should be extended to other separation processes, such as extraction, absorption, etc.

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