FACTUAL DATA BANKS AND THEIR APPLICATION FOR THE SYNTHESIS AND DESIGN OF CHEMICAL PROCESSES AND THE DEVELOPMENT AND TEST OF PHYSICAL PROPERTY ESTIMATION METHODS

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DDBST GmbH Oldenburg

OVERVIEW
"FACTUAL DATA BANKS"

- Context of the Contribution and the Contributor
- Physical Properties and Thermodynamic Models in an "Intelligent" World and their Impact on Technical Development
- Data Banks – From Bibliographic to Factual
- The Dortmund Data Bank
  - Some Facts about the DDB
  - Development and Test of Physical Property Estimation Methods and Parameter Data Banks for Process Simulation
  - Applications for the Synthesis and Design of Chemical Processes
- Conclusion, Acknowledgement

CONTEXT OF CONTRIBUTIONS TO THIS MEETING

Presentations

Group Contribution Methods	Jürgen Gmehling
Data Banks and Application	Jürgen Rarey
Pure Component Property Estimation	Bruce Moller
Ionic Liquids	Jürgen Gmehling

Booth, Poster

Data Bank, Software Presentation	DDBST GmbH
Mod. UNIFAC, PSRK, VTPR	UNIFAC Consortium
Physical Properties from Experiment	LTP GmbH

CONTEXT OF THE CONTRIBUTOR

Research

Industrial Chemistry – University of Oldenburg
Prof. Dr. J. Gmehling - Research Projects, Model Development

UNIFAC Consortium
Mixture Property Estimation

TRU – Durban, SA
Pure Component Property Estimation

CAT - Center for Applied Thermodynamics

Products

DDBST
Data Banks, Software, Consulting

LTP (Associated Institute)
Experimental Services, Consulting

Education

Graduate Courses Thermodynamics, Training Courses DDB/DDBSP
Text books: Industrial Chemistry, Unit Operations, Thermodynamics,

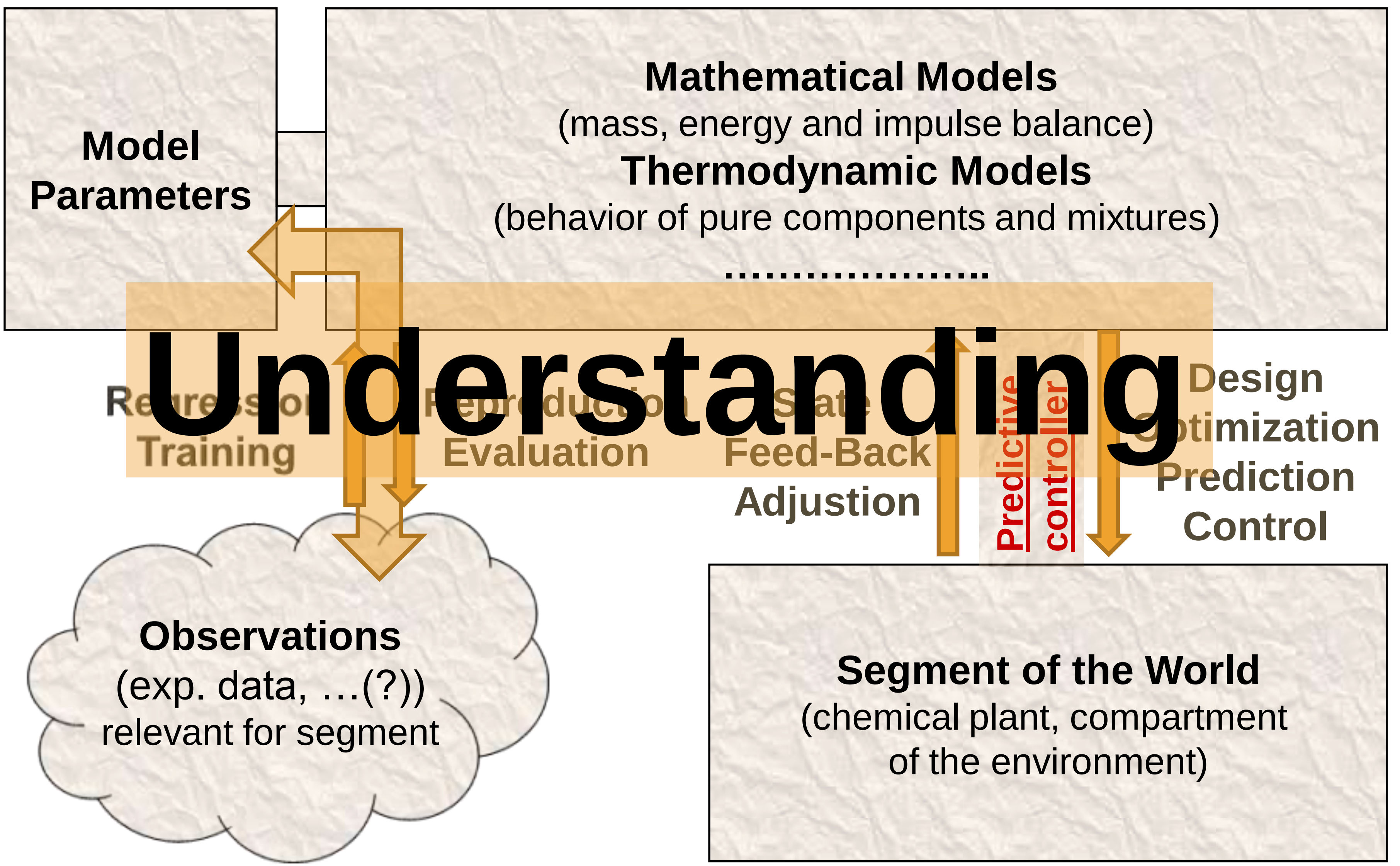
Sales, Marketing, Custom Tailored Products

DECHEMA
Frankfurt, Germany

FIZ CHEMIE
Berlin, Germany

EPCON Int.
Houston, Texas

Mitsubishi Chemical
Kurashiki, Japan


Model Parameters
Mathematical Models
(mass, energy and impulse balance)
Thermodynamic Models
(behavior of pure components and mixtures)
....
Understanding
Regression
Training
Reproduction
Evaluation
State
Feed-Back
Adjustion
Predictive controller
Design
Optimization
Prediction
Control
Observations
(exp. data, …(?))
relevant for segment
Segment of the World
(chemical plant, compartment
of the environment)

IMPORTANCE OF DATA (OBSERVATIONS)

- Engineering, economical, business and political decisions are strongly based on the results of simulation models.
- Results of simulation models are strongly affected by the different assumptions and model parameters.
- Model parameters should be fitted to reliable data (observations) about simplified systems.
- Instead of experimental data, estimation methods or even predictions from first principles can be considered.

SOME DATA BANKS – BIBLIOGRAPHIC TO FACTUAL

Abstracts

Beilstein	1881	
Gmelin	1887	
CAS	1907	

Data Tables and Factual Data Banks

TRC	1942	
NEL (NPL)	1945 (approx.)	
DDB	1973	
DETHERM	1978	combined data input by various groups

Pure Component Parameter Data Banks (incl. Source Data)

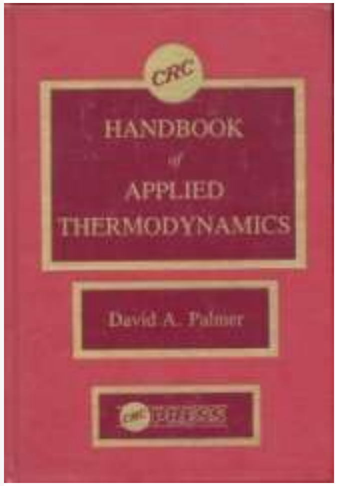
PPDS	1972
DIPPR 801	1980

Mixture Parameter Data Banks

Process simulators, …

II. IMPORTANCE OF PHYSICAL PROPERTIES

It sometimes seems that national security must be threatened to obtain concerted effort by a democratic nation. It was primarily the progress of science that finally ended the war with Japan. An almost forgotten element of the development of the atomic bomb relates to the race between the Allies and Germany to bring it to fruition. There were several ways to develop such a bomb. The short way required knowledge of a physical property of graphite. The Germans guessed at the answer, and guessed incorrectly. As a result they were led on the longer path of development of heavy water in Norway. The Americans knew of the German guess, but measured the physical property. They found that it was substantially different from the guess of the Germans, and were able to devise a much faster route to production of a nuclear weapon.[1,9] If this scenario had been reversed, the U.S. might have become a province of the Third Reich!



Today one of the private competitors

- finds a better entrainer for a separation process.
- is able to use lower number of stages or lower reflux ratio due to more precise phase equilibrium data used for distillation column design.
- uses a specific solvent to improve equilibrium conversion in a chemical reaction
- ....

Better industrial performance using less ressources, less damage to the environment

35 YEARS OF DDB

35 Years

Started 1973 (University of Dortmund, U. Onken and J. Gmehling)

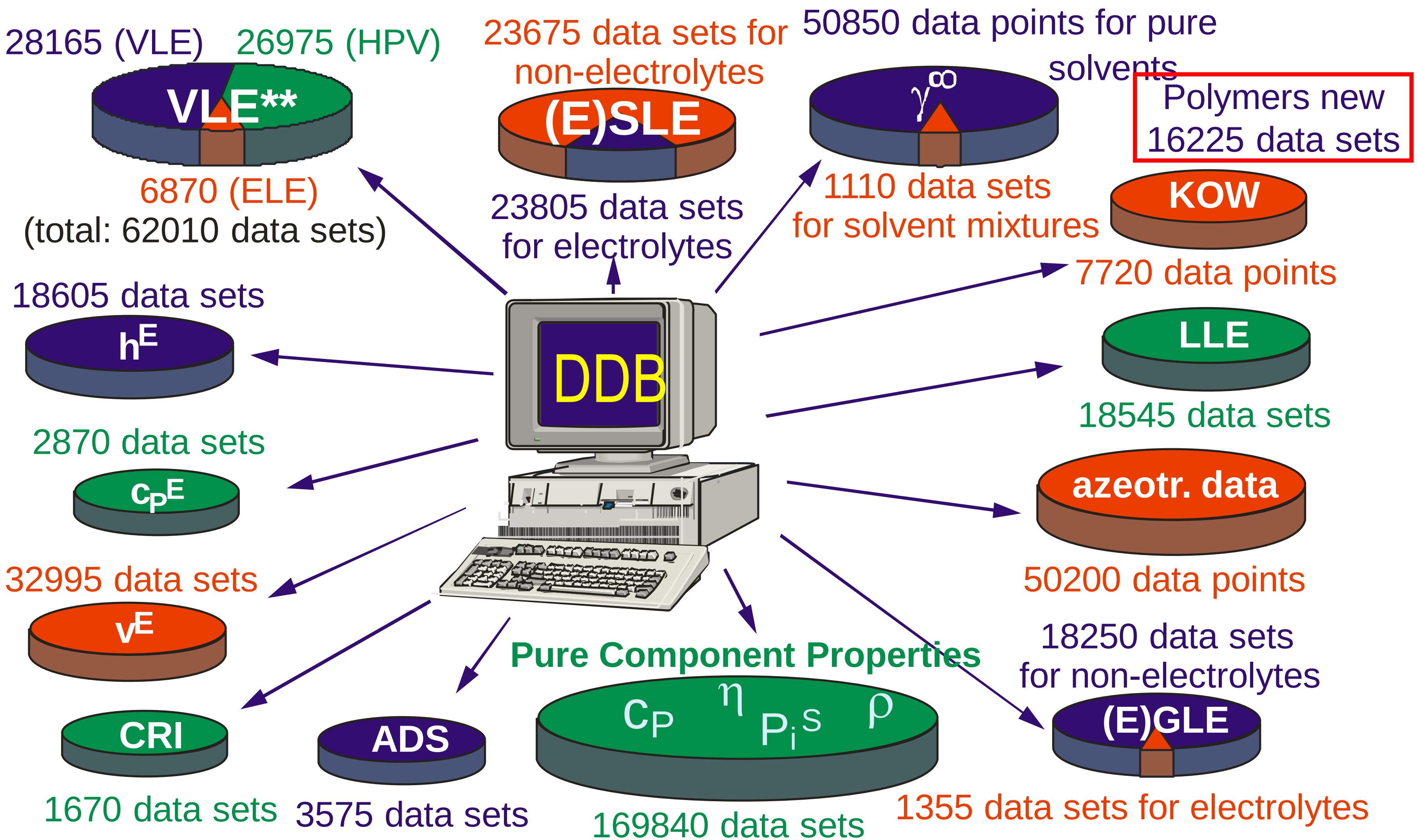
- VLE → UNIFAC group contribution g^E-model
- LLE, h^E, γ^∞, azeotropic data, c_P^E, SLE → mod. UNIFAC
- VLE of low boiling components, GLE → group contribution EOS (PSRK, VTPR)
- VLE, GLE of electrolyte systems, salt solubilities → electrolyte models (LIQUAC, LIFAC)
- PURE → estimation methods for pure component properties
  (in cooperation with groups in Prague, Tallinn, Berlin and Graz)
  (Cordes/Rarey, Nannoolal et al., Moller et al.)
- Polymer data (in cooperation with Prof. Wohlfarth, Merseburg)
- .....

19 Years

1989 - DDBST GmbH

- further development of the DDB.
- software package for data handling, retrieval, correlation, estimation, and visualization as well as process synthesis tools.

THE DDB EXPERIMENTAL DATA FILES (VERSION 2008)



* detailed information is available via internet (www.ddbst.de)

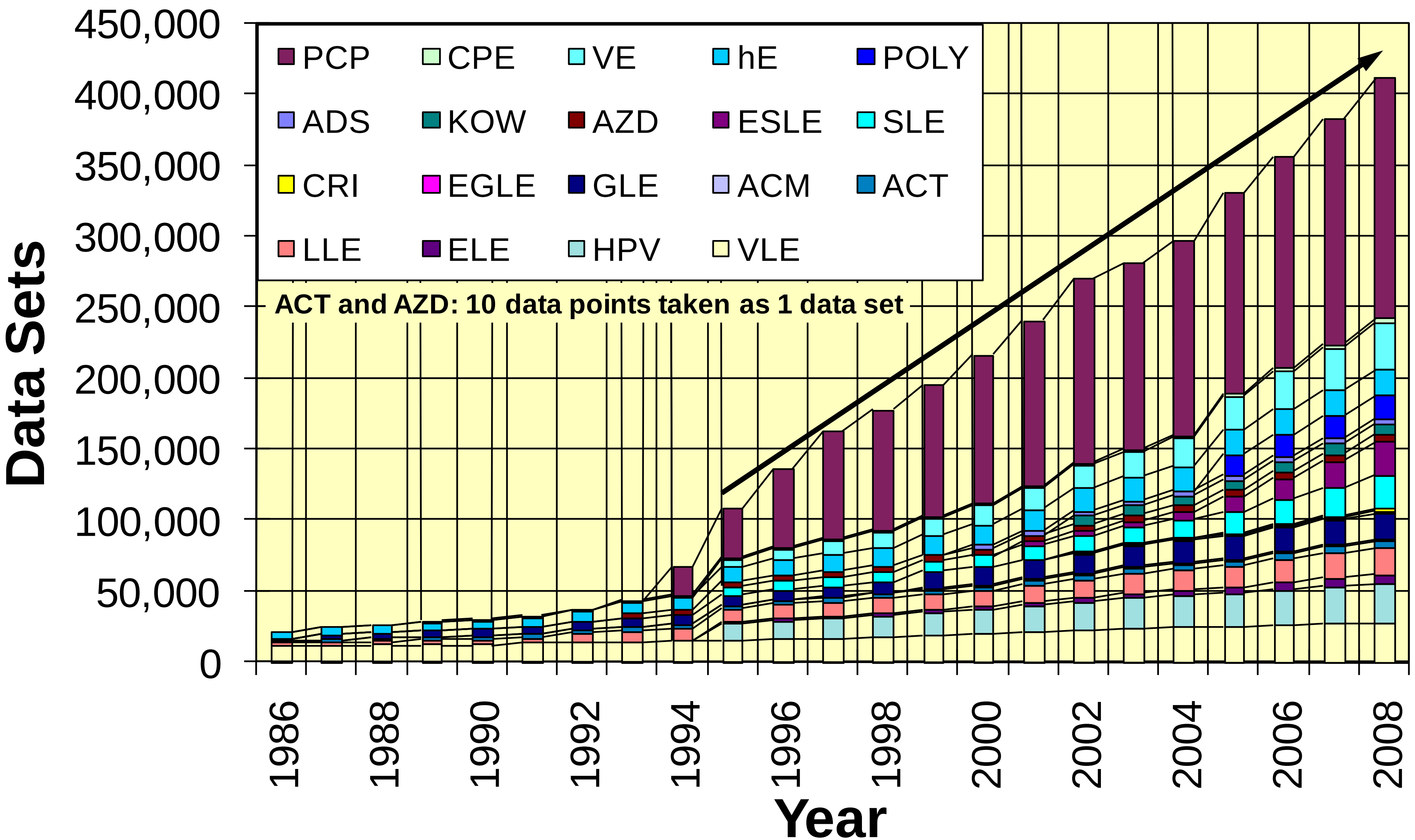
** including unpublished VLE data from chemical companies, e.g. from the former German Democratic Republic

THE DDB DATA 2008

61,000	References
1,800	Journals
28,600	Compounds incl. Salts, Adsorbents and Polymers
21,350	Molecular Structures
47,500	Model Parameters (ParamDB)
104,000	Literature Sources and Documents (LEAR)
2,550	COSMO σ-Profiles

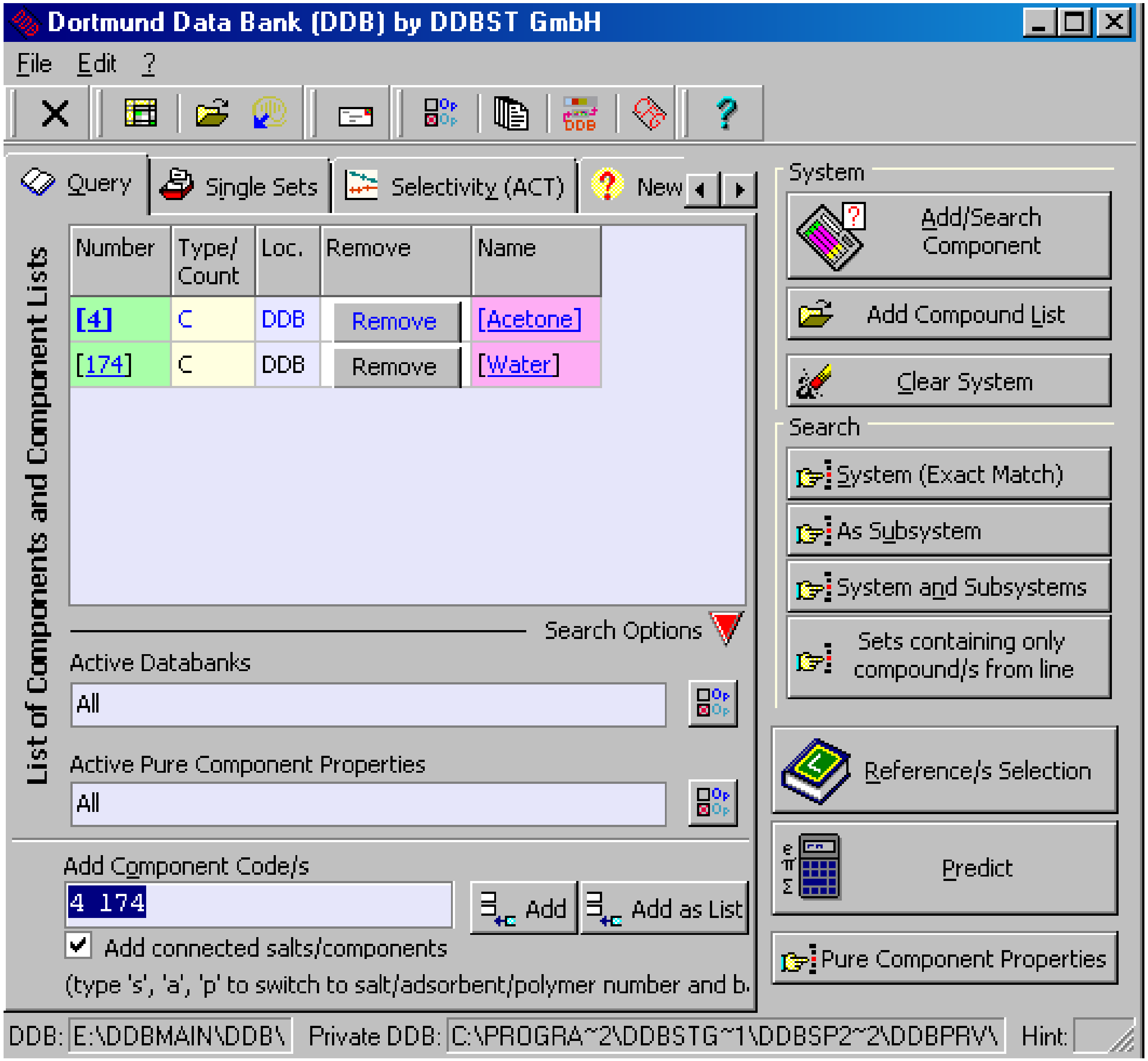
- **Worldwide coverage, all languages**
- **Only experimental data from primary sources**
- **100% of all costs covered, no public funding**
- **Special prices for academia (e.g. British Universities)**

THE DDB – DEVELOPMENT



141 data sets per working day, total costs/year approx. 1.2 Mio. US$

SHORT EXAMPLE ACETONE-WATER



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SHORT EXAMPLE ACETONE-WATER

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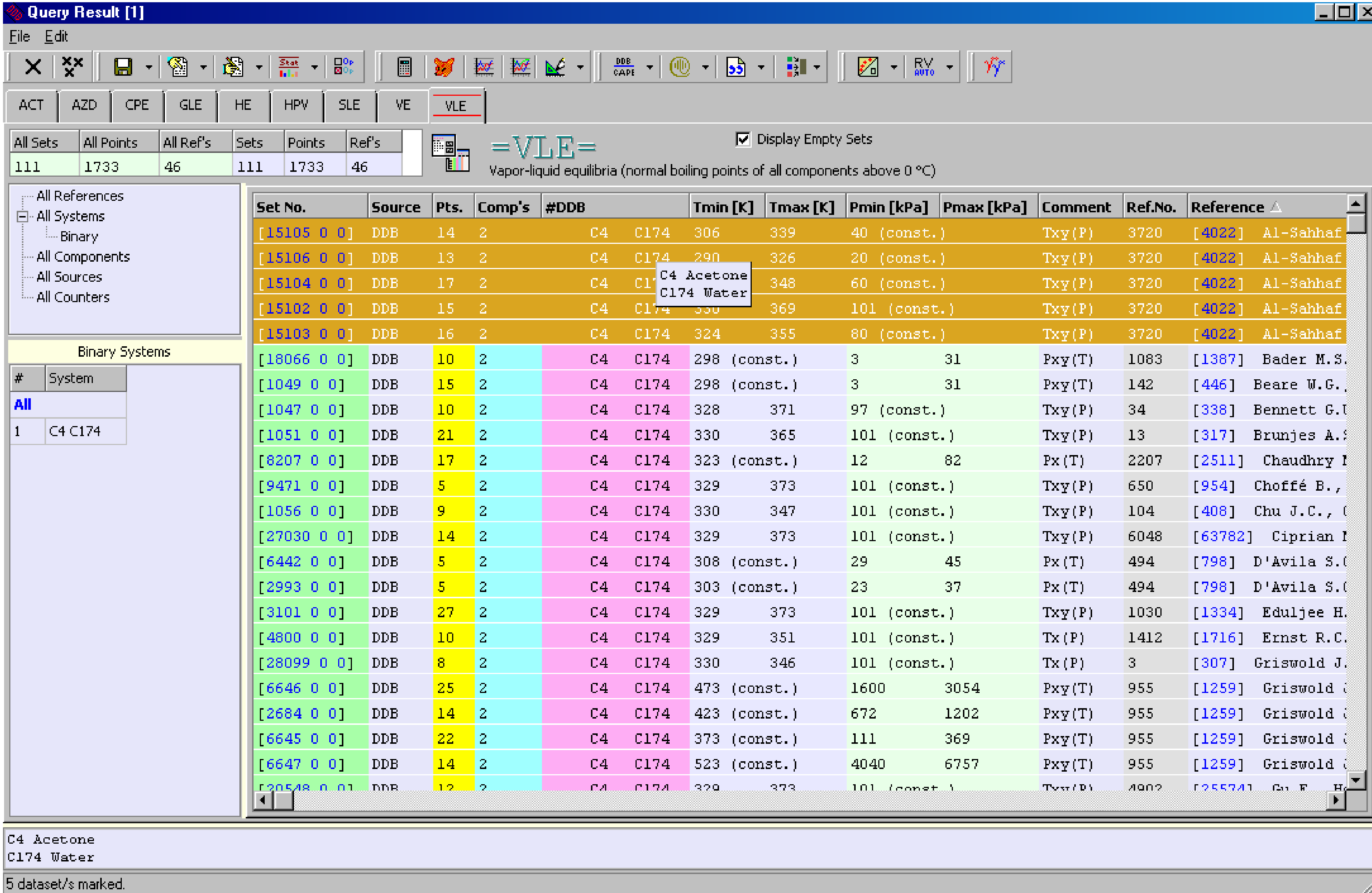
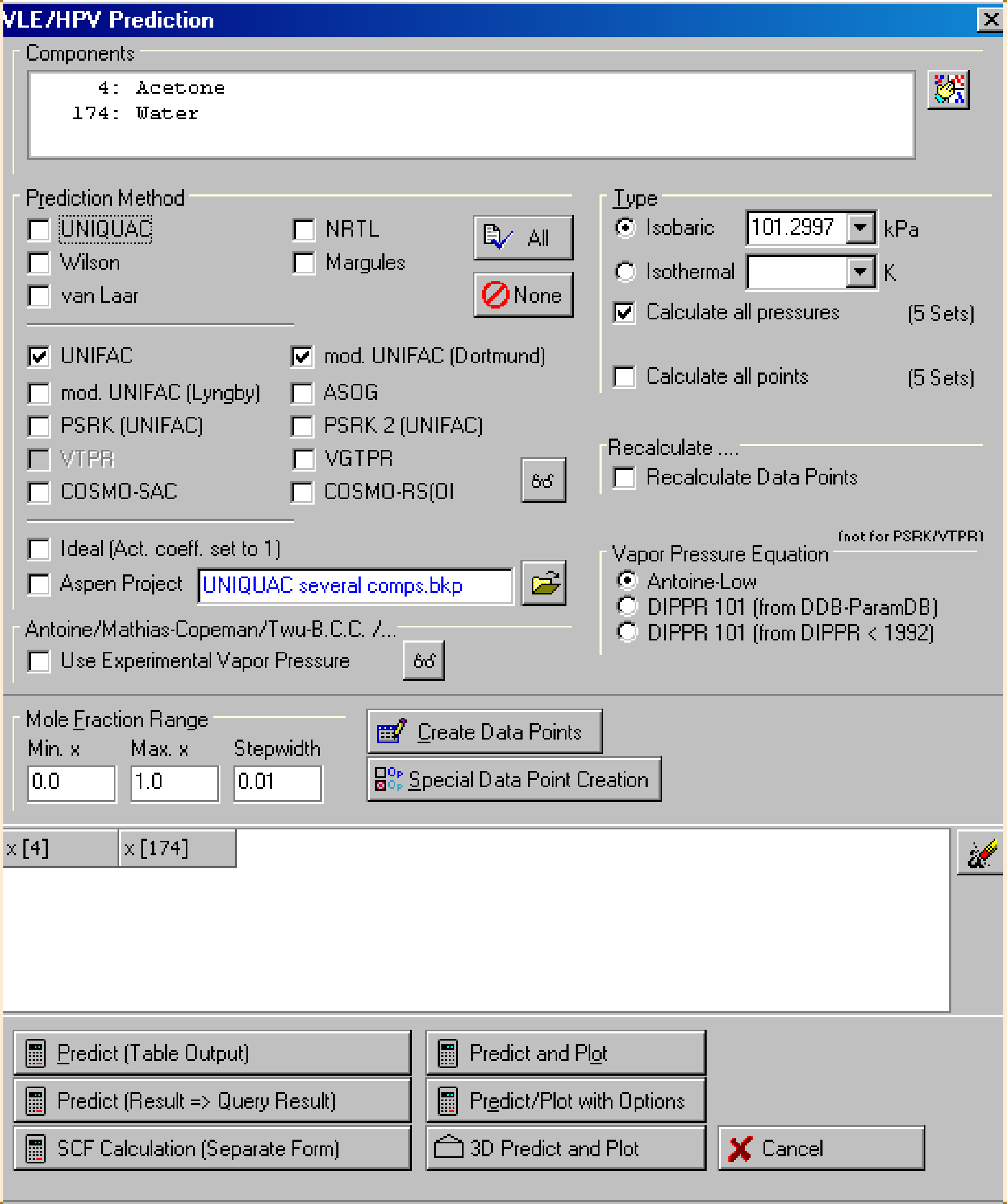
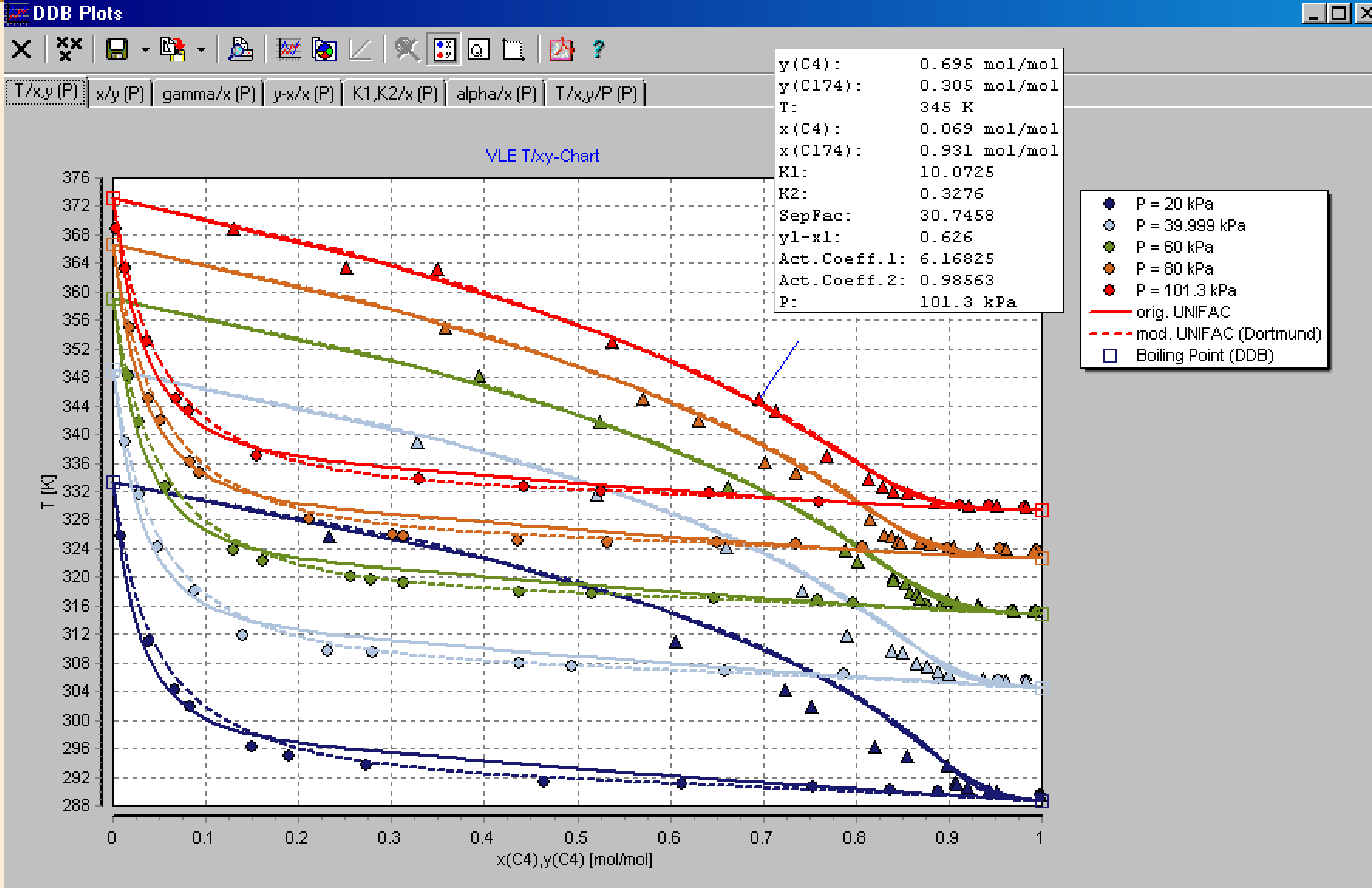


Set No.	Source	Pts.	Comp's	#DDB	Tmin [K]	Tmax [K]	Pmin [kPa]	Pmax [kPa]	Comment	Ref.No.	Reference
[15105 0 0]	DDB	14	2	C4 C174	306	339	40 (const.)		Txy(P)	3720	[4022] Al-Sahhaf
[15106 0 0]	DDB	13	2	C4 C174	290	326	20 (const.)		Txy(P)	3720	[4022] Al-Sahhaf
[15104 0 0]	DDB	17	2	C4 C1[illegible]	[illegible]	348	60 (const.)		Txy(P)	3720	[4022] Al-Sahhaf
[15102 0 0]	DDB	15	2	C4 C174	[illegible]	369	101 (const.)		Txy(P)	3720	[4022] Al-Sahhaf
[15103 0 0]	DDB	16	2	C4 C174	324	355	80 (const.)		Txy(P)	3720	[4022] Al-Sahhaf
[18066 0 0]	DDB	10	2	C4 C174	298 (const.)		3	31	Pxy(T)	1083	[1387] Bader M.S.
[1049 0 0]	DDB	15	2	C4 C174	298 (const.)		3	31	Pxy(T)	142	[446] Beare W.G.,
[1047 0 0]	DDB	10	2	C4 C174	328	371	97 (const.)		Txy(P)	34	[338] Bennett G.[illegible]
[1051 0 0]	DDB	21	2	C4 C174	330	365	101 (const.)		Txy(P)	13	[317] Brunjes A.[illegible]
[8207 0 0]	DDB	17	2	C4 C174	323 (const.)		12	82	Px(T)	2207	[2511] Chaudhry [illegible]
[9471 0 0]	DDB	5	2	C4 C174	329	373	101 (const.)		Txy(P)	650	[954] Choffé B.,
[1056 0 0]	DDB	9	2	C4 C174	330	347	101 (const.)		Txy(P)	104	[408] Chu J.C., [illegible]
[27030 0 0]	DDB	14	2	C4 C174	329	373	101 (const.)		Txy(P)	6048	[63782] Ciprian [illegible]
[6442 0 0]	DDB	5	2	C4 C174	308 (const.)		29	45	Px(T)	494	[798] D'Avila S.[illegible]
[2993 0 0]	DDB	5	2	C4 C174	303 (const.)		23	37	Px(T)	494	[798] D'Avila S.[illegible]
[3101 0 0]	DDB	27	2	C4 C174	329	373	101 (const.)		Txy(P)	1030	[1334] Eduljee H.
[4800 0 0]	DDB	10	2	C4 C174	329	351	101 (const.)		Tx(P)	1412	[1716] Ernst R.C.
[28099 0 0]	DDB	8	2	C4 C174	330	346	101 (const.)		Tx(P)	3	[307] Griswold J.
[6646 0 0]	DDB	25	2	C4 C174	473 (const.)		1600	3054	Pxy(T)	955	[1259] Griswold [illegible]
[2684 0 0]	DDB	14	2	C4 C174	423 (const.)		672	1202	Pxy(T)	955	[1259] Griswold [illegible]
[6645 0 0]	DDB	22	2	C4 C174	373 (const.)		111	369	Pxy(T)	955	[1259] Griswold [illegible]
[6647 0 0]	DDB	14	2	C4 C174	523 (const.)		4040	6757	Pxy(T)	955	[1259] Griswold [illegible]
[20548 0 0]	DDB	12	2	C4 C174	329	373	101 (const.)		Txy(P)	4902	[25574] Gu F. [illegible]


VLE/HPV Prediction
Components
4: Acetone
174: Water
Prediction Method
UNIQUAC
NRTL
All
Wilson
Margules
van Laar
None
UNIFAC
mod. UNIFAC (Dortmund)
mod. UNIFAC (Lyngby)
ASOG
PSRK (UNIFAC)
PSRK 2 (UNIFAC)
VTPR
VGTPR
COSMO-SAC
COSMO-RS(Ol
Ideal (Act. coeff. set to 1)
Aspen Project
UNIQUAC several comps.bkp
Antoine/Mathias-Copeman/Twu-B.C.C. /...
Use Experimental Vapor Pressure
Type
Isobaric
101.2997
kPa
Isothermal
K
Calculate all pressures
(5 Sets)
Calculate all points
(5 Sets)
Recalculate ....
Recalculate Data Points
(not for PSRK/VTPR)
Vapor Pressure Equation
Antoine-Low
DIPPR 101 (from DDB-ParamDB)
DIPPR 101 (from DIPPR < 1992)
Mole Fraction Range
Min. x
Max. x
Stepwidth
0.0
1.0
0.01
Create Data Points
Special Data Point Creation
x [4]
x [174]
Predict (Table Output)
Predict and Plot
Predict (Result => Query Result)
Predict/Plot with Options
SCF Calculation (Separate Form)
3D Predict and Plot
Cancel

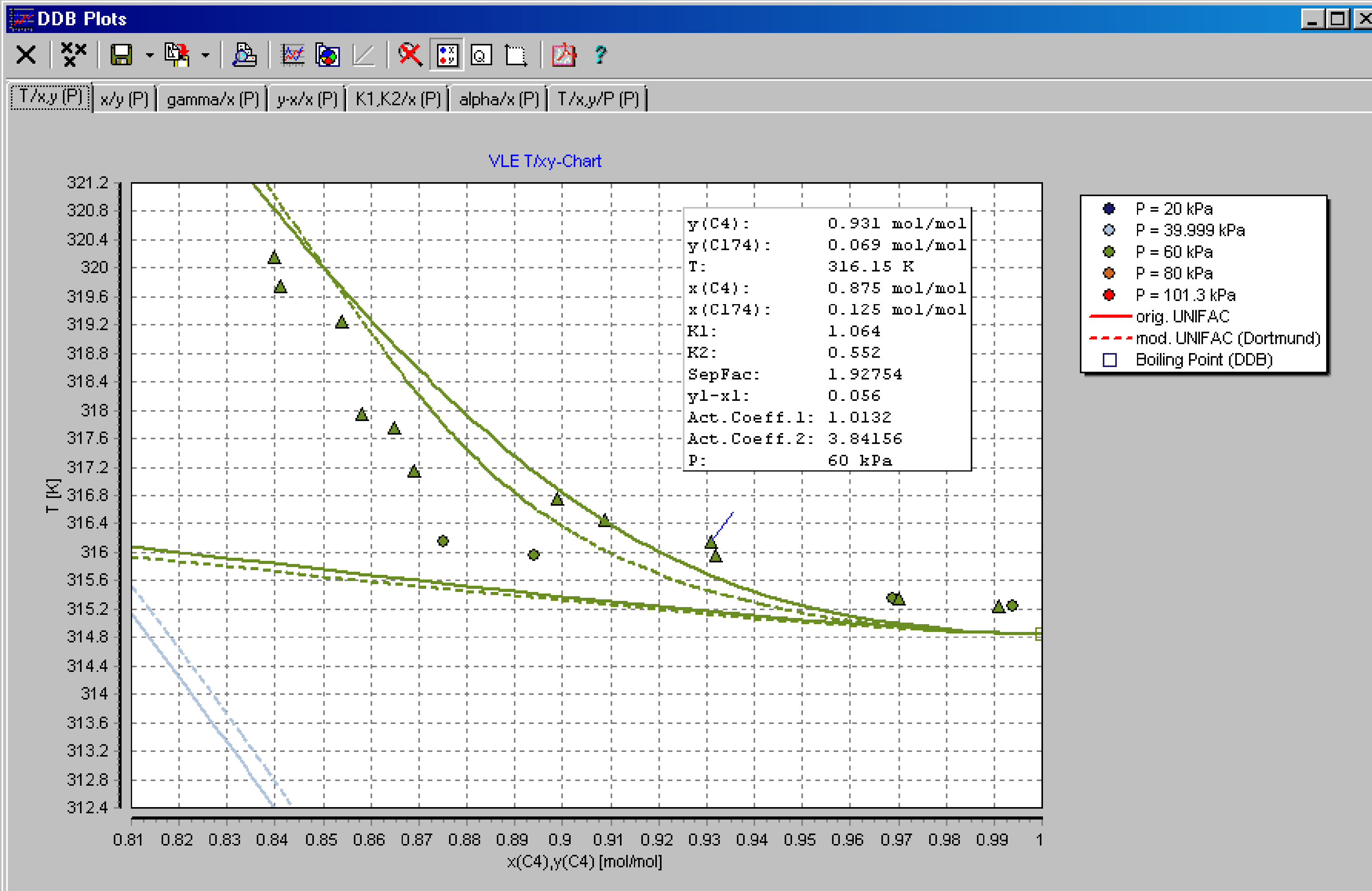


DDB-Number: VLE 15102 [0]
Ref.:[4022] Al-Sahhaf T.A., Jabbar N.J., J.Chem.Eng.Data, 38(4), 522-526, 1993

Components:
(1) C4 Acetone C3H6O
(2) C174 Water H2O

Constant: P = 101.3 kPa

y(C4): 0.695 mol/mol y(C174): 0.305 mol/mol T: 345 K x(C4): 0.069 mol/mol x(C174): 0.931 mol/mol K1: 10.0725 K2: 0.3276 SepFac: 30.7458 y1-x1: 0.626 Act.Coeff.1:



DDB-Number: VLE 15104 [0]
Ref.:[4022] Al-Sahhaf T.A., Jabbar N.J., J.Chem.Eng.Data, 38(4), 522-526, 1993

Components:
(1) C4 Acetone C3H6O
(2) C174 Water H2O

Constant: P = 60 kPa

y(C4): 0.931 mol/mol y(C174): 0.069 mol/mol T: 316.15 K x(C4): 0.875 mol/mol x(C174): 0.125 mol/mol K1: 1.064 K2: 0.552 SepFac: 1.92754 y1-x1: 0.056 Act.Coeff.1:

SOME APPLICATIONS OF THE DDB

Model Development Mixture Properties

UNIFAC, mod. UNIFAC, ASOG	GC g^E-models
PSRK, VTPR	GC EOS-models
LIQUAC, LIFAC	GC electrolyte model
COSMO-RS(OI)	quantum chemical model
GC-COSMO	GC generation of σ-profiles

Activity of complex molecules in common solvents

Solubility of pharmaceuticals and intermediates

Model Development Pure Component Properties

normal boiling temperature

liquid vapor pressure

critical property data

liquid viscosity

liquid vapor pressure (enhanced)

FURTHER APPLICATIONS OF THE DDB

Development of Parameter Data Banks

- Pure component correlations based on various equations
- EOS α-function parameters
- Recommended g^E-model parameters
- Temperature dependent EOS parameters

Process Simulator Integration

- Verifying model parameters prior to process simulation
- Mixture parameter generation for multicomponent mixtures

Process Synthesis

- Prediction of azeotropic points in multicomponent mixtures
- Residual curve construction and constant property lines
- Solvent selection for azeotropic and extractive distillation, extraction,...
- Solvent effects on chemical reaction rates and chemical equilibria
- ...

Dynamic Data Evaluation and Parameter Regression

- Interactive graphical software
- Full documentation of included and discarded data
- Easy upgrade if new data become available
- Easy upgrade by customers using proprietary data
- Comparison to estimation methods
- Multi-property regressions
- …

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VLE OF ACETONE – WATER USING NRTL

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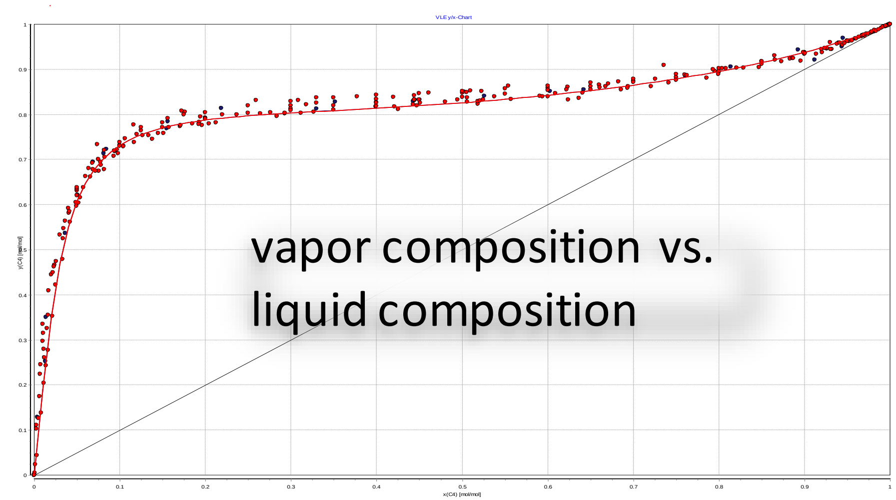
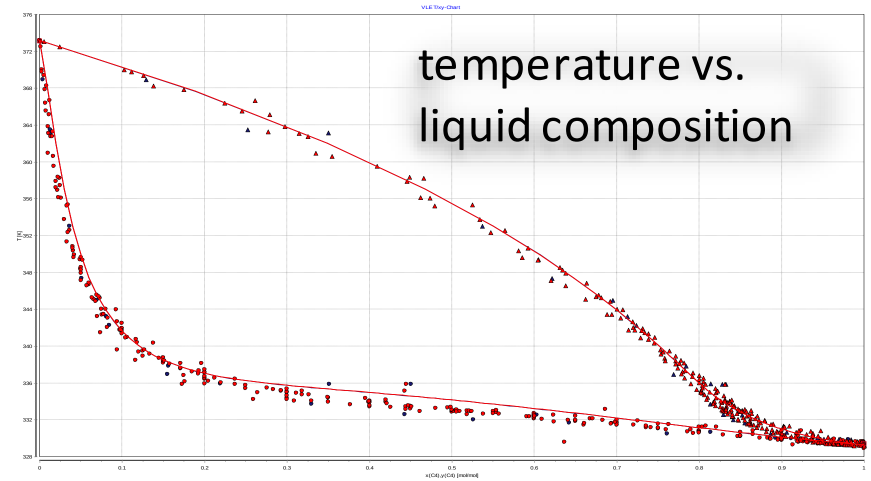
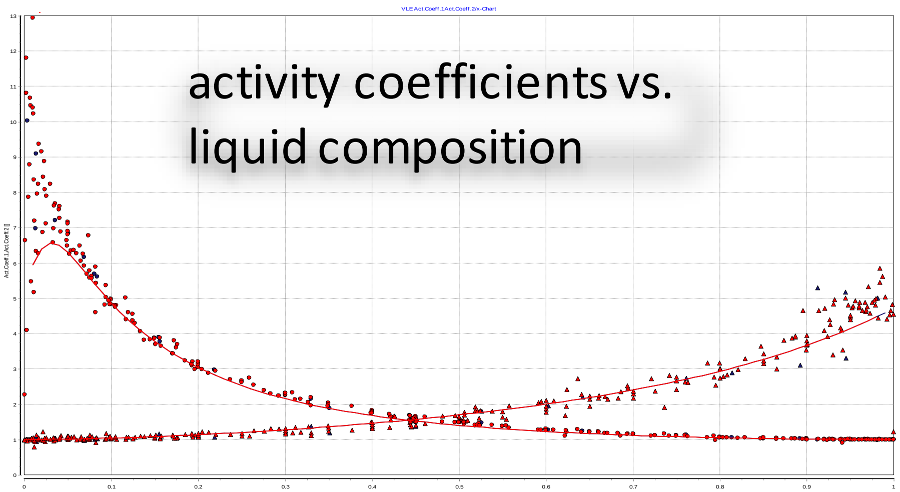
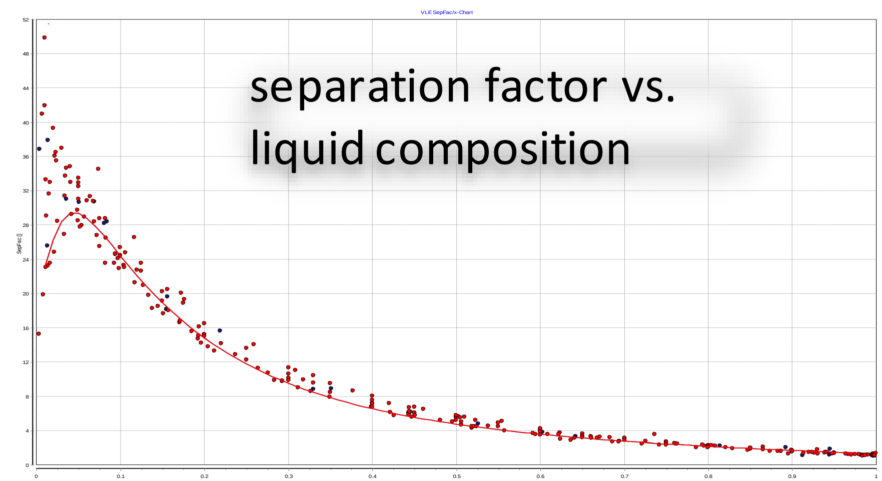




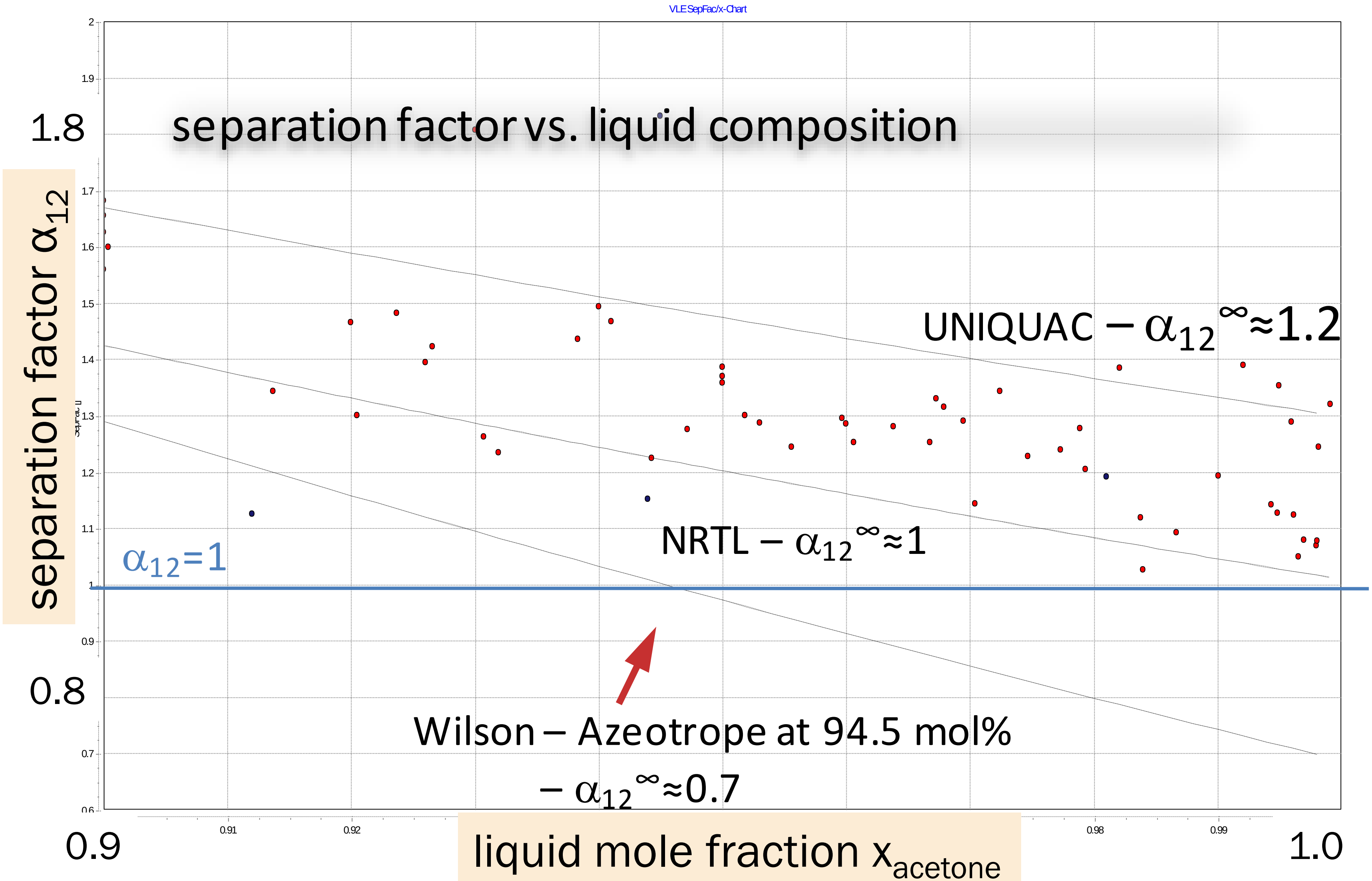




Acetone (1) – Water (2) at 101.3 kPa – data by various authors (DDB)

NRTL using process simulator parameters

VLE OF ACETONE – WATER USING SIMULATOR PARAMETERS



EXPERIMENTAL AND CALCULATED AZEOTROPIC DATA

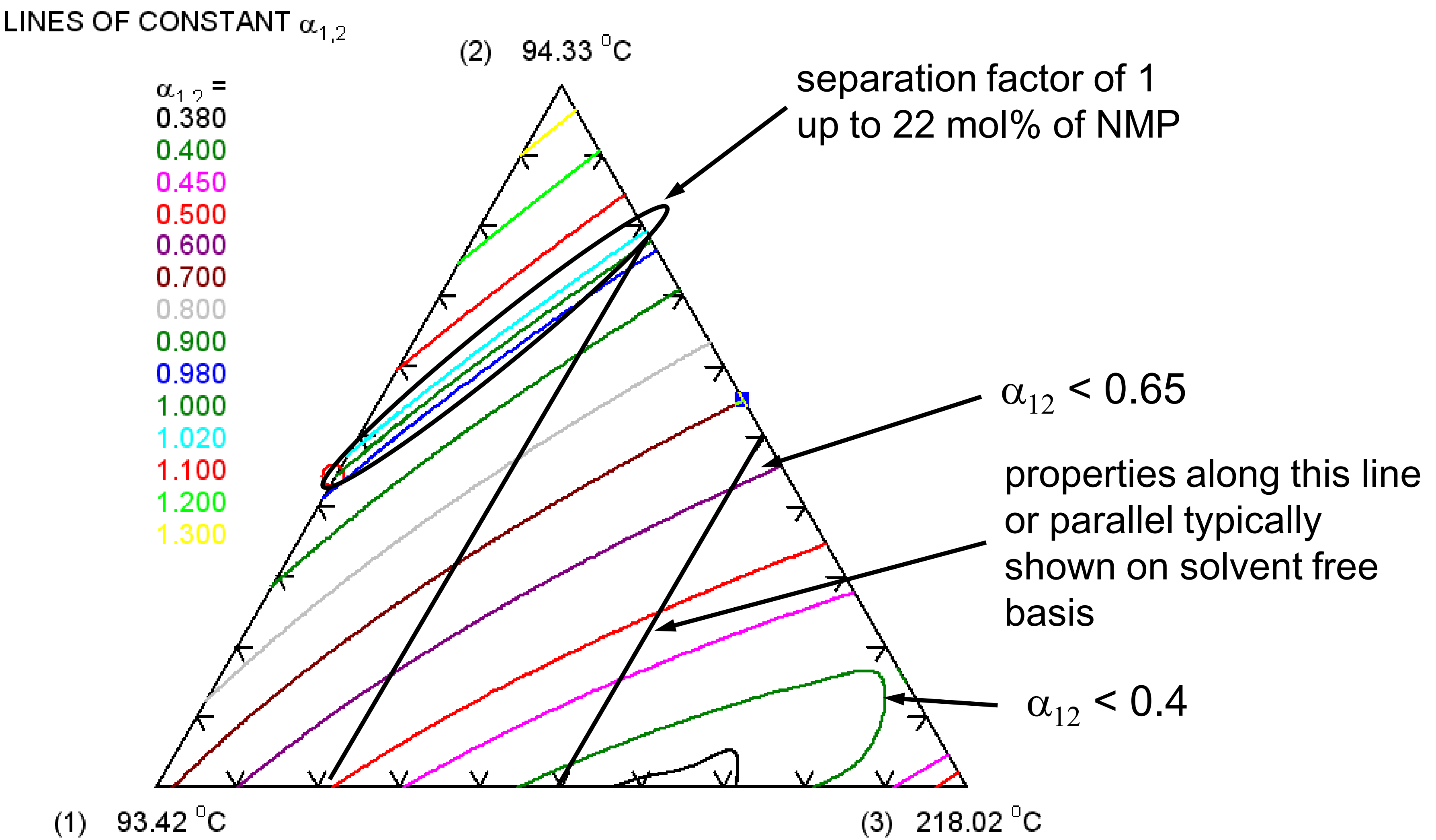
	calc. (NRTL – Aspen 2006.5)				experimental*			
system	type of azeotrope	ϑ / °C	$y_{1,az}$	$y_{2,az}$	type of azeotrope	ϑ / °C	$y_{1,az}$	$y_{2,az}$
1-2	homPmax	77.5	0.550		homPmax	77.6	0.543	
1-3	none				none			
1-4	homPmax	67.7	0.554		homPmax	67.9	0.552	
2-3	homPmax	53.5		0.233	homPmax	53.2		0.248
2-4	homPmax	64.9		0.559	homPmax	64.8		0.553
3-4	none				none			
1-2-3	none				none			
1-2-4	homPmax	64.7	0.116	0.461	homPmax	64.9	0.113	0.462
1-3-4	none				none			
2-3-4	none				none			
1-2-3-4	none				n.a.			

Benzene (1) - Cyclohexane (2) - Acetone (3) - Ethanol (4) at P = 101.325 kPa

* mean values of the experimental data stored in the Dortmund Data Bank

n.a.: not available

CONSTANT PROPERTY LINES



Benzene (1) – Cyclohexane (2) – NMP (3) at 101.3 kPa (UNIFAC)

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CONSTANT PROPERTY LINES

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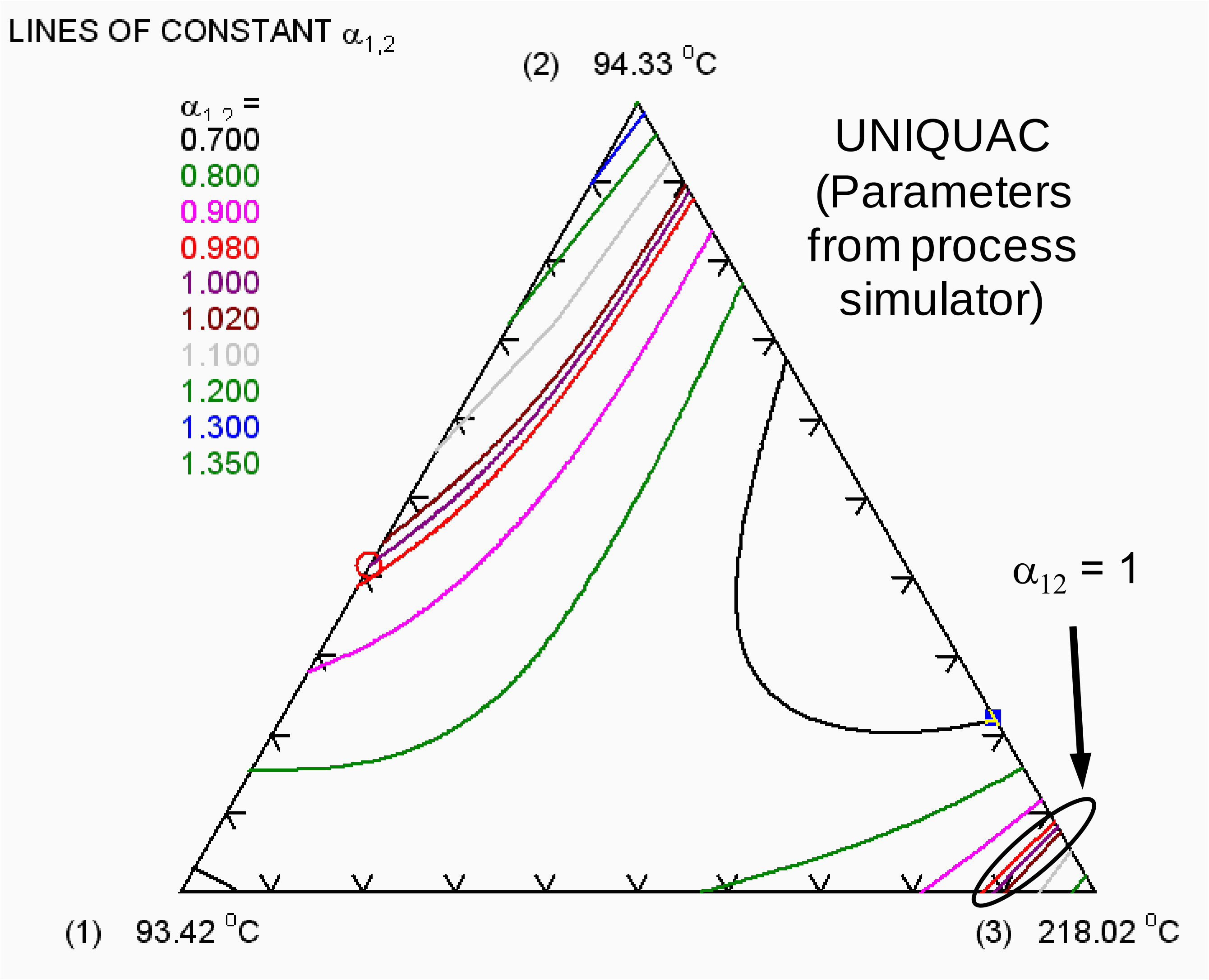
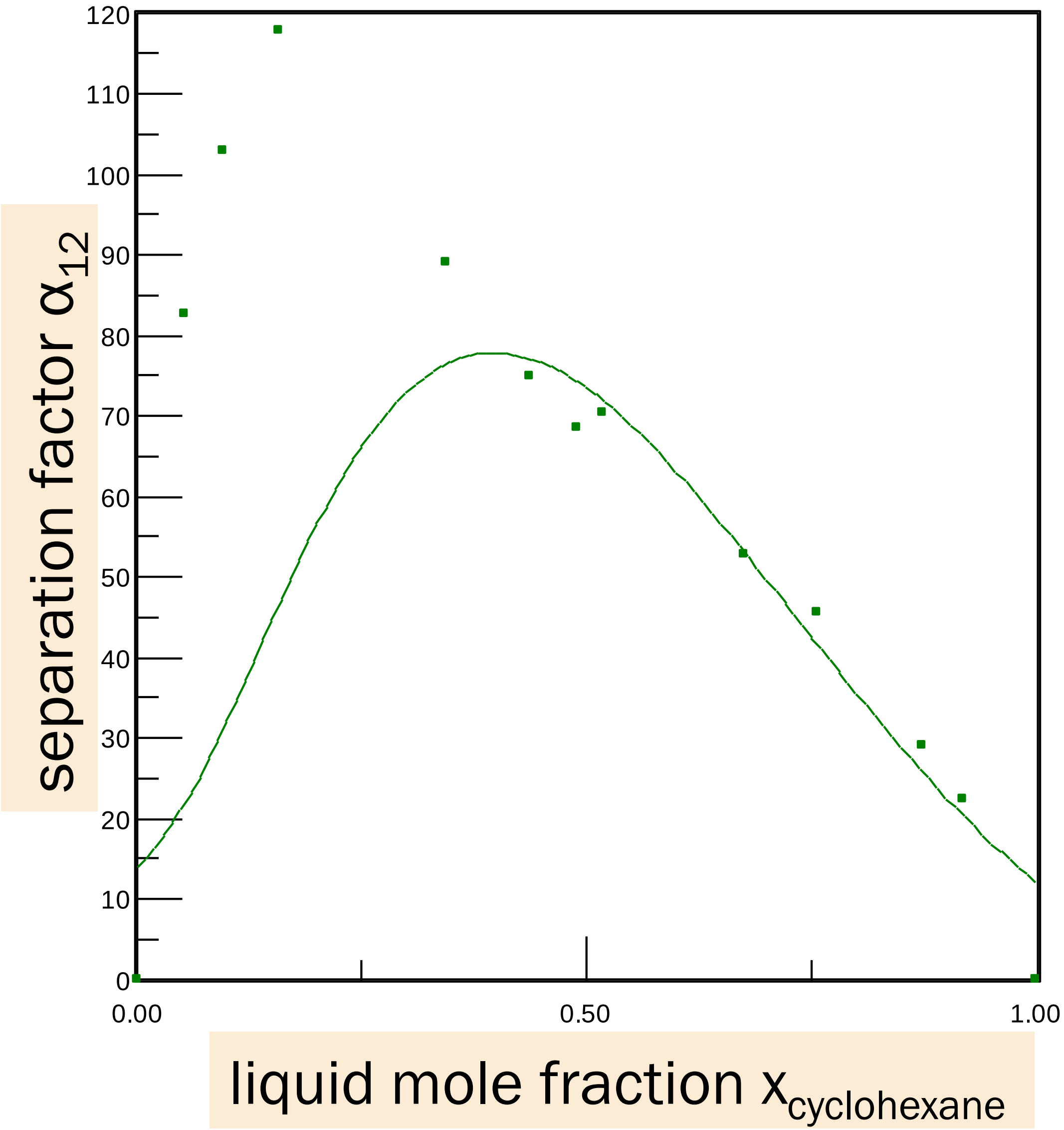


THE FLAW........



Separation factor α_{12} in the system Cyclohexane (1) – NMP (2) at 101.3 kPa (UNIQUAC, parameters from a process simulator)

WHERE ARE WE NOW?

The “Promise” of Process Simulation

- evaluation of process alternatives
- virtual experiments, innovative concepts
- ...

The Reality

- used for gradual improvement, optimization
- sustained development, little discontinuous innovation

Potential of Thermodynamic Data Banks and Predictive Methods

- Data Mining
- New Solutions to Problems
- Technological “Leaps”
- ...

data mining - "the nontrivial extraction of implicit, previously unknown, and potentially useful information from data"

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ENTRAINER SELECTION
BY DATA OR PARAMETER MINING

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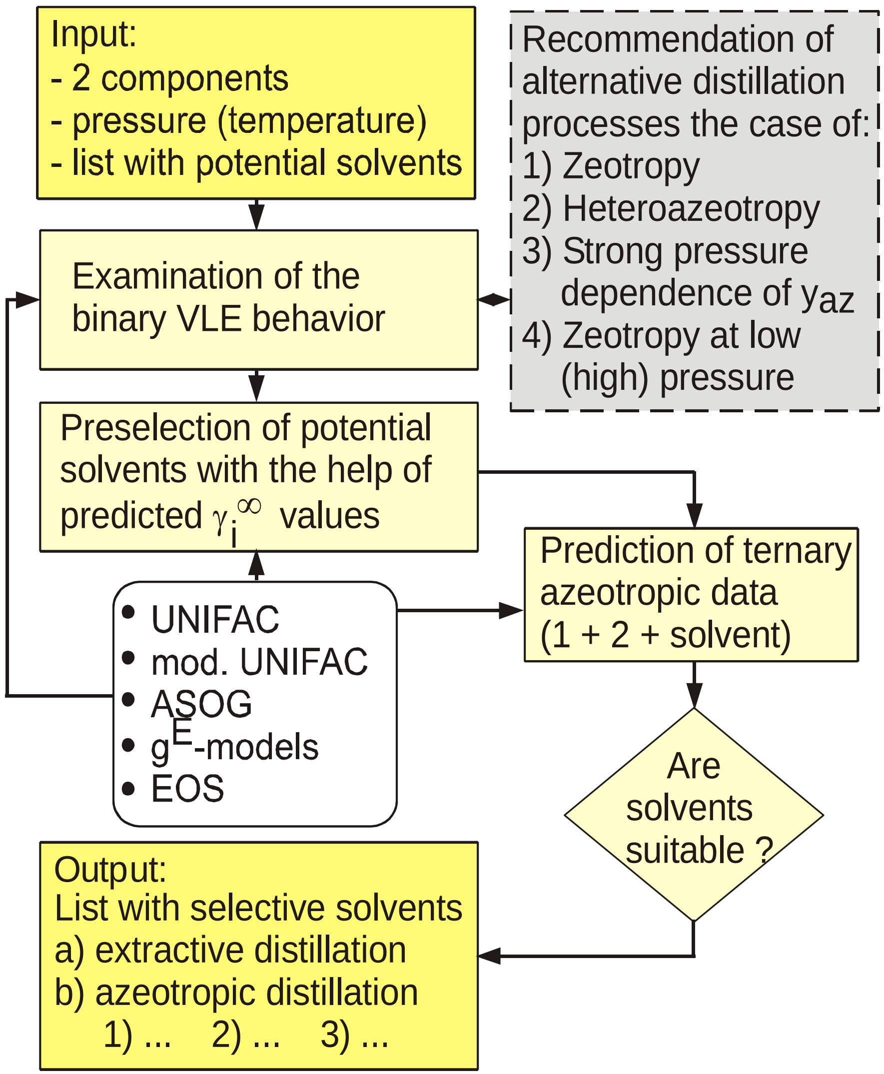
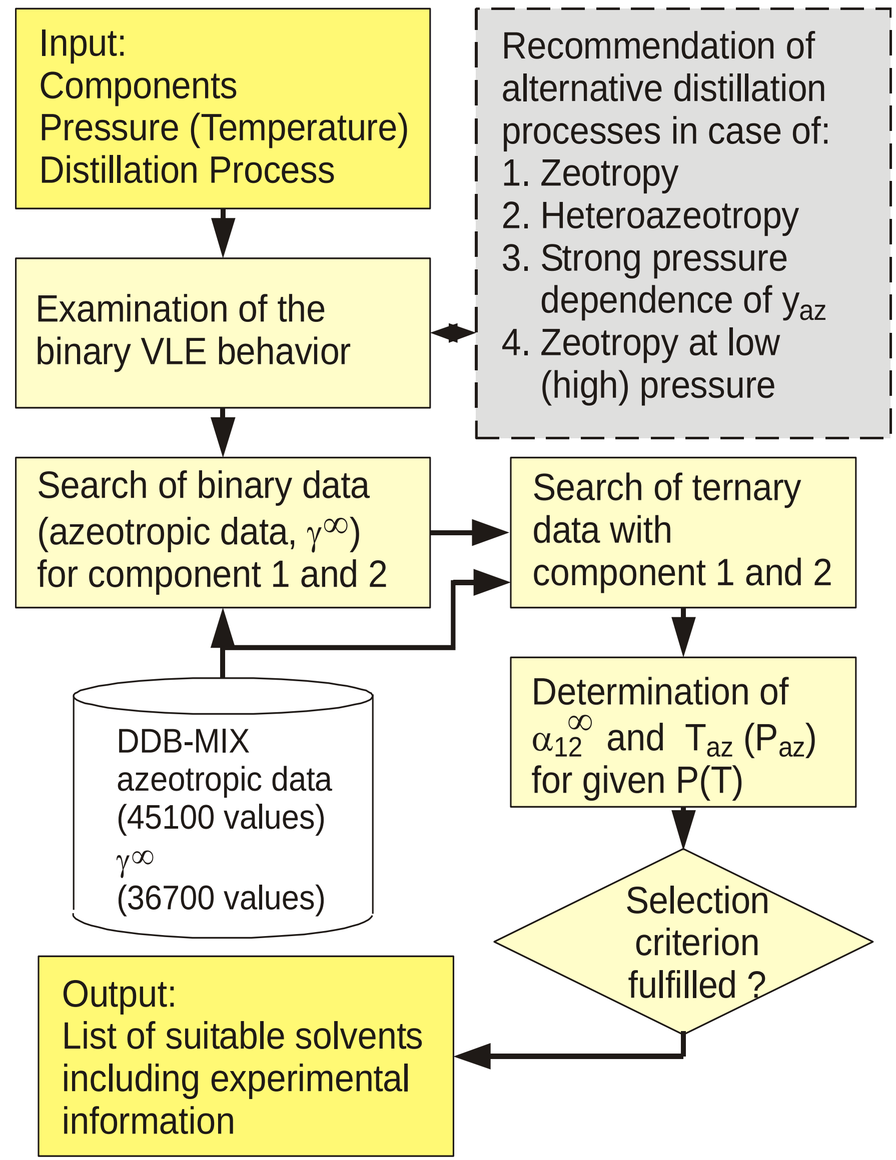
Selective_Solvent_Models_DDB.cdr 22.08.2001





TYPICAL RESULT FOR THE SEARCH OF SELECTIVE SOLVENTS USING A THERMODYNAMIC MODEL

components to be separated: (1) VINYL

P = 101.325 kPa T_b(1) = 345 ...

azeotropic data for system (1 ...

model : modified UNIFAC (...

list of solvents introducing n... ...iner)

(1) VINYL ACETATE (2) METHANOL
extractive distillation
modified UNIFAC (Dortmund)
P = 101.325 kPa

sel. solvent (3)	$\alpha(1,2)^\infty$
ANILINE	0.360
DIBUTYL ETHER	0.194
DECANE	0.146
DODECANE	0.171
BUTYL ACETATE	0.270
1-HEXADECENE	0.208
2-HEPTANONE	0.386
BUTYLBENZENE	0.142
....	....

T_b [K]	α(1...	types of azeotropes introduced (1)-(3)	(2)-(3)	(1)-(2)-(3)	T_m(3) [K]
		none	none	none	266.85
		none	none	none	175.30
		none	none	none	243.45
		none	none	none	263.59
		none	none	none	199.70
		none	none	none	277.55
		none	none	none	237.65
		none	none	none	185.25
		none	none	none	189.15
		none	none	none	304.09
		none	none	none	291.15
		none	none	none	308.95
		none	none	none	314.05
		none	none	none	279.02
		none	none	none	225.35
		none	none	none	286.35
		none	none	none	195.15
		none	none	none	222.50
		none	none	none	242.00
		none	none	none	217.65
419.47		none	none	none	240.15
438.15		none	none	none	181.15
.....		...	...	...	.....

minimum ΔT_b (entrainer - binary mixture) = 40.00 [K]

minimum α(1,2 or inverse) at infinite dilution = 1.5

CONCLUSION

- Factual data and data estimation methods are of great practical importance
- Development and regular update of a large factual data bank is possible in a free market environment without public funding
- Inadequate physical properties are the major reason for unrealistic results of process simulation and customer frustration
- Factual data banks and predictive methods combined with appropriate data mining tools carry a huge potential for economic and technological progress

ACKNOWLEDGEMENT

Prof. Dr. Jürgen Gmehling

Coworkers of DDBST GmbH

PhD Students and Researchers

....

The Audience