A New Approach for Reliable Computation of Homogeneous Azeotropes in Multicomponent Mixtures

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Computing Homogeneous Azeotropes

- Why
  - Identify limitations in separation operations
  - Construction of residue curve maps for design and synthesis of separation operations
  - Evaluation of thermodynamic models
- How
  - Solve system(s) of nonlinear equations derived from equifugacity condition
  - These equation system(s) often have multiple and/or trivial roots, or may have no solutions

Formulation : Simultaneous Approach

$$x_i \left(\ln P - \ln P_i^{sat} - \ln \gamma_i \right) = 0, \; i \in \mathcal{C}$$

$$1 - \sum_{i \in \mathcal{C}} x_i = 0$$

- $\mathcal{C}$ is the set of all N components
- Ideal vapor phase
- P_i^{sat} and γ_i are functions of T
- All k-ary azeotropes $(k \leq N)$ are solutions, as are all of the pure components (trivial roots)
- Need solution method guaranteed to find all solutions

Formulation : Sequential Approach

- If $x_i \neq 0$

$$\ln P - \ln P_i^{sat} - \ln \gamma_i = 0,\ i \in \mathcal{C}_{nz}$$

$$1 - \sum_{i \in \mathcal{C}_{nz}} x_i = 0$$

- $\mathcal{C}_{nz}$ is a set of k nonzero components
- All k-ary azeotropes $(k \leq N)$ for the chosen $\mathcal{C}_{nz}$ are solutions; there may be no solutions
- Solve (unordered) sequence of problems :

  For k $= 2 \rightarrow$ N:

  For all combinations of k nonzero components, solve for all k-ary azeotropes

- Need solution method guaranteed to find all solutions of all problems, and to determine with certainty when there are no solutions

Formulation : Other Issues

- T dependence of γ_i
  - Treat explicitly using T-dependent parameters in γ_i model
  - Guess a reference temperature T_{ref} and treat T-dependent parameters as constants evaluated at T_{ref} $\Rightarrow$ No guarantee all azeotropes will be found, even if equations solved correctly

- Solutions of equifugacity equations may not be stable phases (liquid may split)
  - Need to check stability of liquid phase at azeotropic composition and temperature
  - Interval analysis also provides guaranteed method to determine stability (Stadtherr $et\ al.$, 1994)

Some Current Solution Methods

- Various local methods — Fast, but initialization dependent and hard to find all roots

- Fidkowski $et\ al.$ (1993) use a homotopy-continuation method
  - Simultaneous approach with explicit T-dependence of γ_i
  - Improved reliability but no guarantee that all roots are found

- Harding $et\ al.$ (1997) use a branch and bound method
  - Simultaneous and sequential approaches, but T_{ref} approach for T-dependence of γ_i
  - Reformulation as a global optimization problem using convex underestimating functions
  - Mathematical guarantee that all roots are found

Interval Approach

- Interval Newton/Generalized Bisection (IN/GB)
  - Given a system of equations to solve, an initial interval (bounds on all variables), and a solution tolerance
  - IN/GB can find

    with mathematical and computational certainty

    either all the solutions or that no solutions exist. (e.g., Kearfott 1987,1996; Neumaier 1990)

- A general purpose approach : requires no simplifying assumptions or problem reformulations

- Details of algorithm given by Schnepper and Stadtherr (1996)

- Implementation based on modifications of routines from INTBIS and INTLIB packages (Kearfott and coworkers)

Example Problems

- Solved using both simultaneous and sequential approaches (with same results for azeotropic composition and temperature)

- Solved for case of T-dependent γ_i-model parameters and for the case of constant γ_i-model parameters

- Problem 1
  - Ethanol, Methyl Ethyl Ketone, Water
  - 1 atm, 10-100 °C, Wilson Equation

- Problem 2
  - Acetone, Chloroform, Methanol
  - 16.8 atm, 100-200 °C, NRTL Equation

- Problem 3
  - Acetone, Methyl Acetate, Methanol
  - 1 atm, 10-100 °C, Wilson Equation

- Times reported for Sun Ultra 1/140

Results - Problem 1

Azeotropes

γ_i parameters	E	MEK	W	T (°C)
Constant (T_{ref}=73.7 °C)	0.49	0.51	0.00	74.1
	0.90	0.00	0.10	78.1
	0.00	0.68	0.32	73.7
	0.23	0.54	0.23	72.8
T-dependent	0.49	0.51	0.00	74.1
	0.91	0.00	0.09	78.2
	0.00	0.68	0.32	73.7
	0.23	0.54	0.23	72.8

CPU Times (sec)

	Constant	T dependent
Sequential	0.21	0.34
Simultaneous	0.90	4.62

E = Ethanol; MEK = Methyl Ethyl Ketone
W = Water

Results - Problem 2

Azeotropes

γ_i parameters	A	C	M	T (°C)
Constant	0.33	0.67	0.00	181.8
(T_{ref}=152.4°C)	0.29	0.00	0.71	155.3
	0.00	0.41	0.59	151.6
T-dependent	0.32	0.68	0.00	181.2
	0.29	0.00	0.71	155.4
	0.00	0.41	0.59	151.6

CPU Times (sec)

	Constant	T dependent
Sequential	0.51	0.82
Simultaneous	0.94	6.15

A = Acetone; C = Chloroform; M = Methanol

Results - Problem 3

Azeotropes

γ_i parameters	A	MA	M	T (°C)
Constant*	0.53	0.47	0.00	55.7
	0.75	0.00	0.25	54.5
	0.00	0.68	0.32	54.4
	0.27	0.47	0.26	54.3
T dependent	0.66	0.34	0.00	55.6
	0.79	0.00	0.21	55.4
	0.00	0.66	0.34	53.6

CPU Times (sec)

	Constant	T dependent
Sequential	0.40	1.04
Simultaneous	1.63	6.36

A = Acetone(1); MA = Methyl Acetate(2)
M=Methanol(3)

* $\Lambda_{12} = 0.480$, $\Lambda_{21} = 1.550$, $\Lambda_{13} = 0.768$
$\Lambda_{31} = 0.566$, $\Lambda_{23} = 0.544$, $\Lambda_{32} = 0.650$

Concluding Remarks

- Have solved many other problems using Wilson, NRTL and UNIQUAC activity coefficient models with up to N=5

- Interval analysis provides an efficient, general purpose approach for solving azeotrope problems, providing a mathematical and computational guarantee of reliability

- Interval analysis provides powerful problem solving techniques with many other applications in the modeling of phase behavior and in other process modeling problems

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