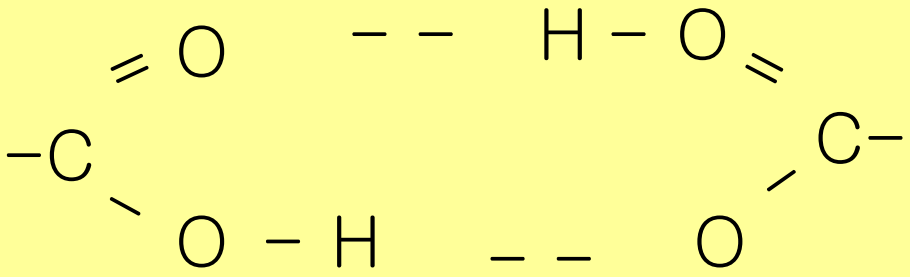
Motivations

- Mixtures with organic acids have presented difficulties for an EOS approach
- Recently developed association models are still not adequate for mixtures with organic acids in EOS frames
- The possibility of the extension and the application of Veytsman statistics (1990) was investigated

Introduction

- Organic acids generally form dimers in vapor phase



- The dimer formations are long been considered only in vapor phase

EOS with Specific Interaction Approaches

- Chemical theories : APACT used different hydrogen bonding parameters in each phases
- Physical theories : SAFT denoted a large single associative site for dimer formations
- Quasichemical theories : NLF-HB EOS cannot describe the dimer formations explicitly

The Composition of Veytsman Statistics

- Donors and acceptors distribution

$$\prod_i \frac{N_d^i!}{N_{i0}!} \prod_j \frac{N_a^i!}{N_{0j}!} \prod_i \prod_j \frac{1}{N_{ij}!}$$

- The probability for an acceptor to be placed the HB location of a donor

$$\frac{1}{N_r}$$

- The Veytsman statistics

$$\prod_i \frac{N_d^i!}{N_{i0}!} \prod_j \frac{N_a^i!}{N_{0j}!} \prod_i \prod_j \frac{1}{N_{ij}!} \frac{1}{N_r^{N_{HB}}} \exp\left(-\sum_i \sum_j \beta N_{ij} A_{ij}\right)$$

Lattice Partition Function

$$\Omega = \Omega_{PHYS}\ \Omega_{HB}$$

- Ω_{PHYS} : You et al. (1994)
- Ω_{HB} : Proposed extension of Veytsman statistics for both dimers and n-mers

$$\Omega_{HB} = \frac{N_{10}^{D0}!(2!)^{N_{11}^{H0}}}{N_{10}^{D}!(2!)^{N_{11}^{H}}} \prod_{i=1}^{M} \frac{N_{i0}^{H0}!}{N_{i0}^{H}!} \prod_{j=1}^{N} \frac{N_{0j}^{H0}!}{N_{0j}^{H}!} \prod_{i=1}^{M} \prod_{j=1}^{N} \frac{N_{ij}^{H0}!}{N_{ij}^{H}!} (P_{ij})^{(N_{ij}^{H} - N_{ij}^{H0})} \exp(-\beta A_{ij}^{H} N_{ij}^{H})$$

$$P_{ij} = N_{rH} / N_r^2 = (N_0 + r_H \sum_{i=1}^{M} N_d^i + r_H \sum_{j=1}^{N} N_a^j) / N_r^2$$

- P_{ij} : Proposed probability of finding an acceptor site j around donor site i for a loosely connected pair ij

  ✓ For j to be adjacent to i
  (1) acceptor j must find a specific site (= $1/N_r$) and
  (2) the site is not occupied by physically interacting groups (= N_{rH}/N_r)

Thermodynamic Properties

- Pressure and chemical potentials

$$P_{HB} = (kT/V_H)\nu_{HB}\rho\left(2 - \frac{N_r}{N_{rH}}\right)$$

$$\frac{\mu_i^{HB}}{kT} = \frac{\nu_{HB}\rho N_r r_{Hi}}{N_{rH}} - \ln\frac{N_{10}^{D0}}{N_{10}^{D}} - \sum_{k=1}^{M} d_k^i \ln\frac{N_{k0}^{HB}}{N_{k0}^{HB0}} - \sum_{k=1}^{N} a_k^i \ln\frac{N_{0k}^{HB}}{N_{0k}^{HB0}}$$

$$\nu_{HB} = \sum_i^M \sum_j^N (N_{ij}^H - N_{ij}^{H0}) / \sum_{i=1}^C r_i N_i \qquad \rho = \sum_{i=1}^C r_i N_i / N_r \qquad r_{Hi} = r_H(\sum_{k=1}^M d_k^i + \sum_{k=1}^N a_k^i) - r_i$$

$$(2N_{11}^H)(N_d^1 - 2N_{11}^H)(N_a^1 - 2N_{11}^H) = (N_{10}^H N_{01}^H)^2 \exp(-\beta A_{ij}^H) N_{rH} / N_r^2$$

$$N_{ij}^H = N_{i0}^H N_{0j}^H \exp(-\beta A_{ij}^H) N_{rH} / N_r^2$$

- The physical parts are given by You et al. (1994)

Physical Parameters

- The coordination number : $z = 10$
- Lattice volume : $V_H = 9.75\ cm^3/mol$
- Pure parameters (r_i, ε_{ii}) : Fitted to saturated liquid density and vapor pressure and correlated ($T_0 = 298.15\ K$)

$$r_i = r_a + r_b(T - T_0) + r_c[T\ln(T_0/T) + T - T_0]$$

$$\varepsilon_{ii}/k = e_a + e_b(T - T_0) + e_c[T\ln(T_0/T) + T - T_0]$$

- Binary parameter (λ_{ij}) : Regressed from VLE data

$$\varepsilon_{12} = (\varepsilon_{11}\ \varepsilon_{22})^{1/2}(1-\lambda_{12})$$

Hydrogen Bonding Parameters

- The segment number of donors and acceptors : $r_H = 0.05$

$$A^H_{ii} = U^H_{ii} - TS^H_{ii}$$

$$A^H_{ij} = (A^H_{ii} A^H_{jj})^{(1/2)}$$

$$A^H_{ij} = (0.5 A^H_{ii} A^H_{jj})^{(1/2)} \quad (\textit{ for solvation with acid })$$

System	U^H_{ii}/k(K)	S^H_{ii}/k
Alcohol	-3082	-1.86
Water	-1626	-2.00
Acid	-5370	-4.38
Amine	-1670	-1.26

Temperature Coefficients of Physical Parameters

Chemicals	e_a	e_b	e_c	r_a	r_b	r_c	Range(K)
Propane	84.774	0.0161	-0.1399	6.827	-0.0005	0.0077	115-345
N-Butane	90.844	0.0242	0.0023	8.362	-0.0014	0.0029	280-405
N-Pentane	94.484	0.0369	0.0189	9.924	-0.0021	0.0012	303-443
N-Hexane	97.278	0.0313	-0.0245	11.460	-0.0015	0.0061	273-473
N-Heptane	99.068	0.0352	-0.0187	13.035	-0.0019	0.0060	273-513
N-Decane	101.689	0.0529	0.0125	17.805	-0.0034	0.0057	368-598
Methanol	134.046	0.0626	-0.2178	2.859	-0.0025	0.0008	223-483
Ethanol	120.628	0.0184	-0.2085	4.326	-0.0038	0.0039	249-489
1-Propanol	118.806	-0.0133	-0.1821	5.844	-0.0047	-0.0038	256-517
1-Butanol	117.716	-0.0107	-0.1220	7.459	-0.0050	-0.0049	284-544
1-Pentanol	117.027	-0.0082	-0.0992	8.980	-0.0030	0.0027	273-573
Acetic acid	140.713	0.0735	0.0874	5.090	-0.0019	-0.0088	298-569
Propionic acid	132.068	0.0448	0.0527	6.631	-0.0009	-0.0015	292-582
Pentanoic acid	126.562	0.0268	-0.0149	10.013	-0.0067	-0.0177	303-623
Water	372.129	-0.4030	0.1231	1.811	0.0001	-0.0028	273-493
Ethylamine	107.762	0.0092	-0.0838	4.872	-0.0012	0.0014	192-442
Butylamine	111.101	0.0149	-0.0347	8.127	-0.0004	-0.0064	224-514

Comparison of the Present Model with Data

System	T(K)	λ_{12}	AADP	AADY	System	T(K)	λ_{12}	AADP	AADY
Propane + methanol	310.7	0.032	1.859	0.0073	Methanol + ethanol	298.15	0.013	1.030	0.0213
Propane + ethanol	325.0 – 350.0	-0.020 – -0.043	6.982	0.0189	Methanol + 1-propanol	333.17	0.029	0.320	0.0232
N-Butane + methanol	323.15 – 373.15	0.029 – 0.047	2.008	0.0285	Methanol + water	298.15 – 473.15	-0.187 - -0.041	2.645	0.0181
N-Pentane + 1-propanol	313.15	0.020	1.591	0.0059	Ethanol + 1-propanol	323.15 – 353.15	0.029 – 0.032	0.388	0.0233
N-Pentane + 1-pentanol	303.15	0.014	5.495	0.0006	Ethanol + water	323.15	-0.141	1.295	0.0074
N-Hexane + ethanol	298.15 – 328.15	0.002 – 0.014	1.115	0.0289	1-Propanol + water	363.15	-0.074	0.864	0.0099
N-Hexane + 1-propanol	338.15	0.017	2.149	0.0097	Acetic acid + propionic acid	313.15	0.006	1.211	0.0144
N-Heptane + acetic acid	293.15 – 313.15	0.052 – 0.057	2.747	0.0194	Water + acetic acid	293.15 – 363.05	-0.183 - -0.133	0.733	0.0104
N-Heptane + pentanoic acid	373.15	0.019	1.536	0.0072	Water + propionic acid	313.15 – 323.15	-0.138 - -0.131	3.854	0.0146
N-Decane + 1-propanol	368.15	0.004	3.079	0.0154	Ethylamine + ethanol	293.15	-0.199	3.235	0.0053
N-Decane + 1-butanol	358.15 – 388.15	0.008 – 0.010	1.253	0.0037	Butylamine + 1-propanol	328.15	-0.100	1.713	0.0056
Avg.								2.141	0.0136

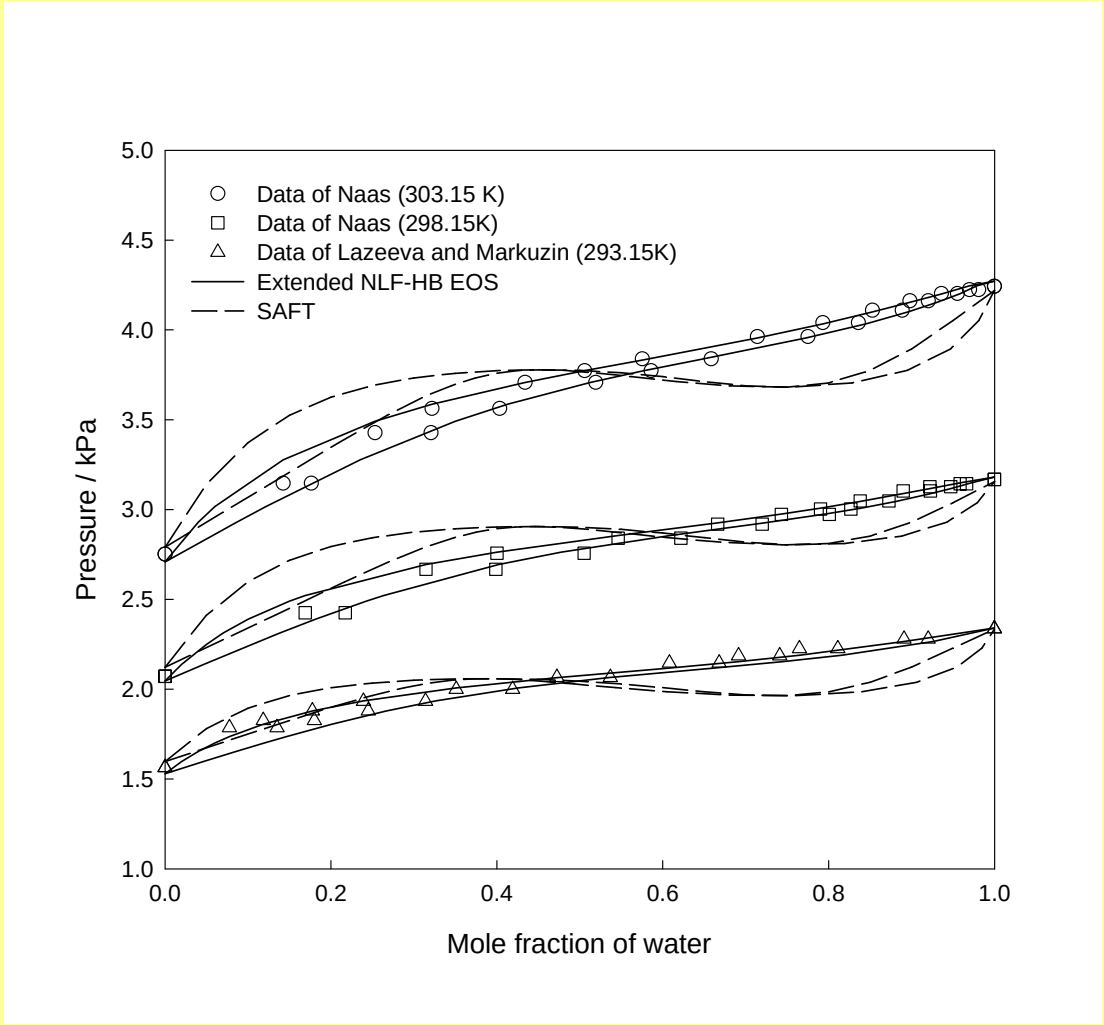


Figure. Comparison of present results and SAFT with experimental data for water + acetic acid at different temperatures

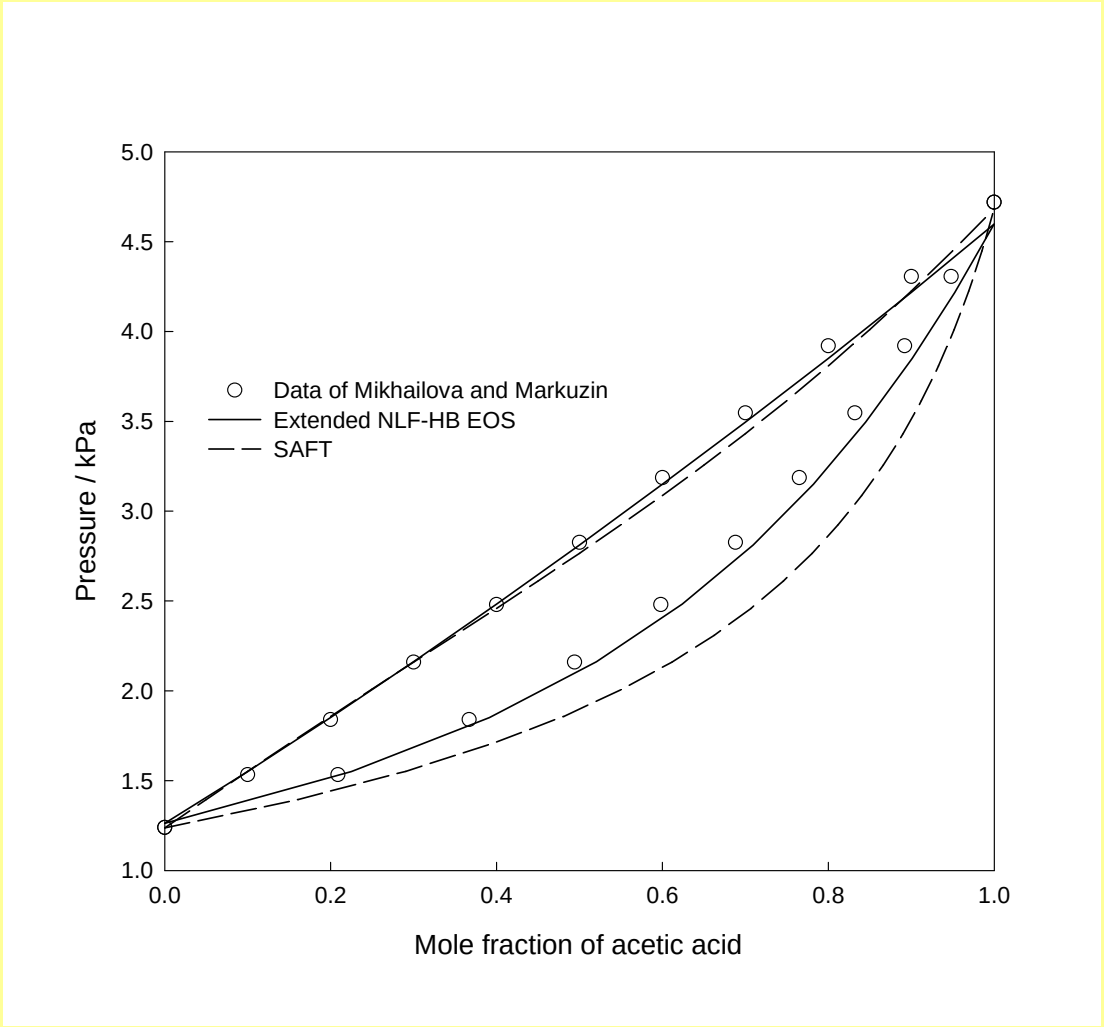


Figure. Comparison of present results and SAFT with experimental data for acetic acid + propanoic acid at 313.15 K

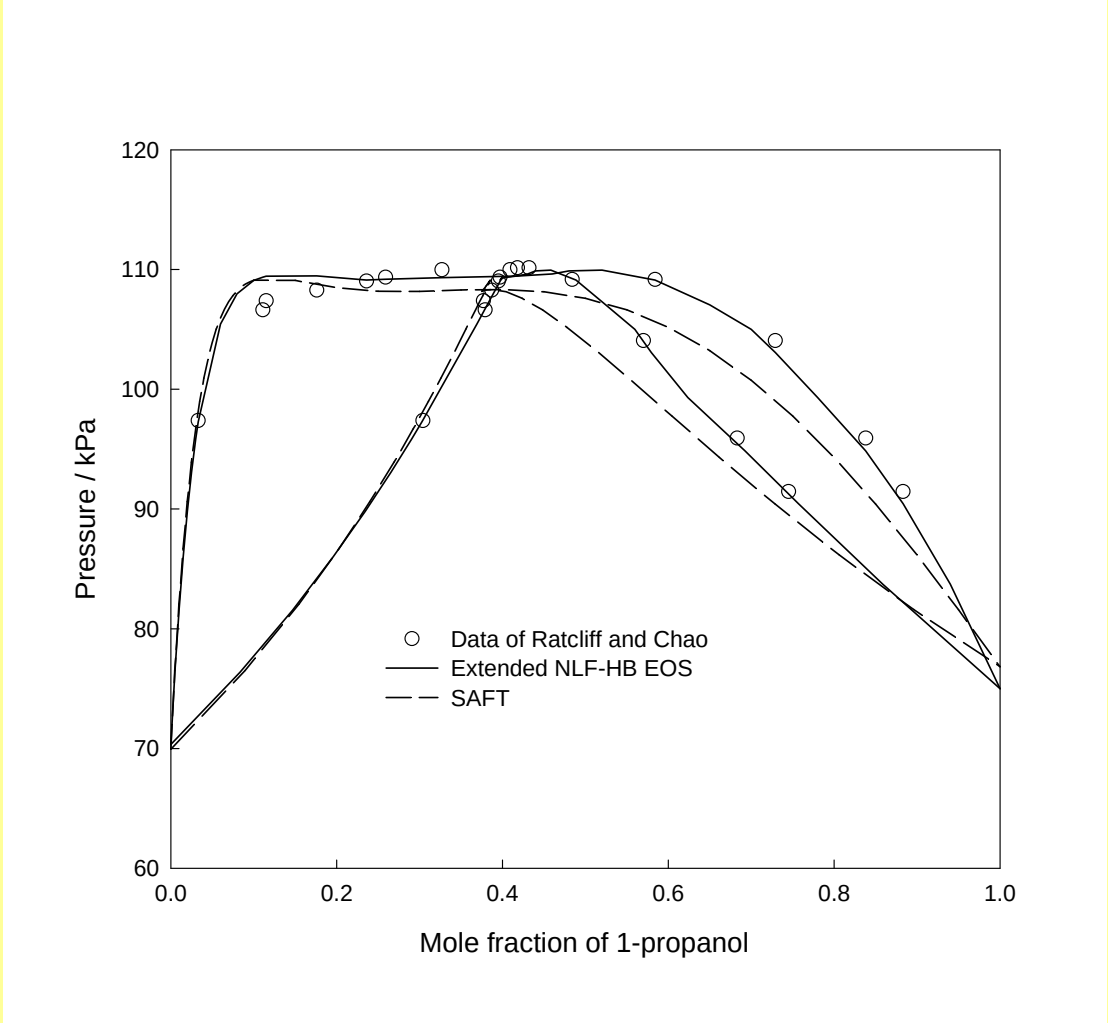


Figure. Comparison of present results and SAFT with experimental data for 1-propanol + water at 363.15 K

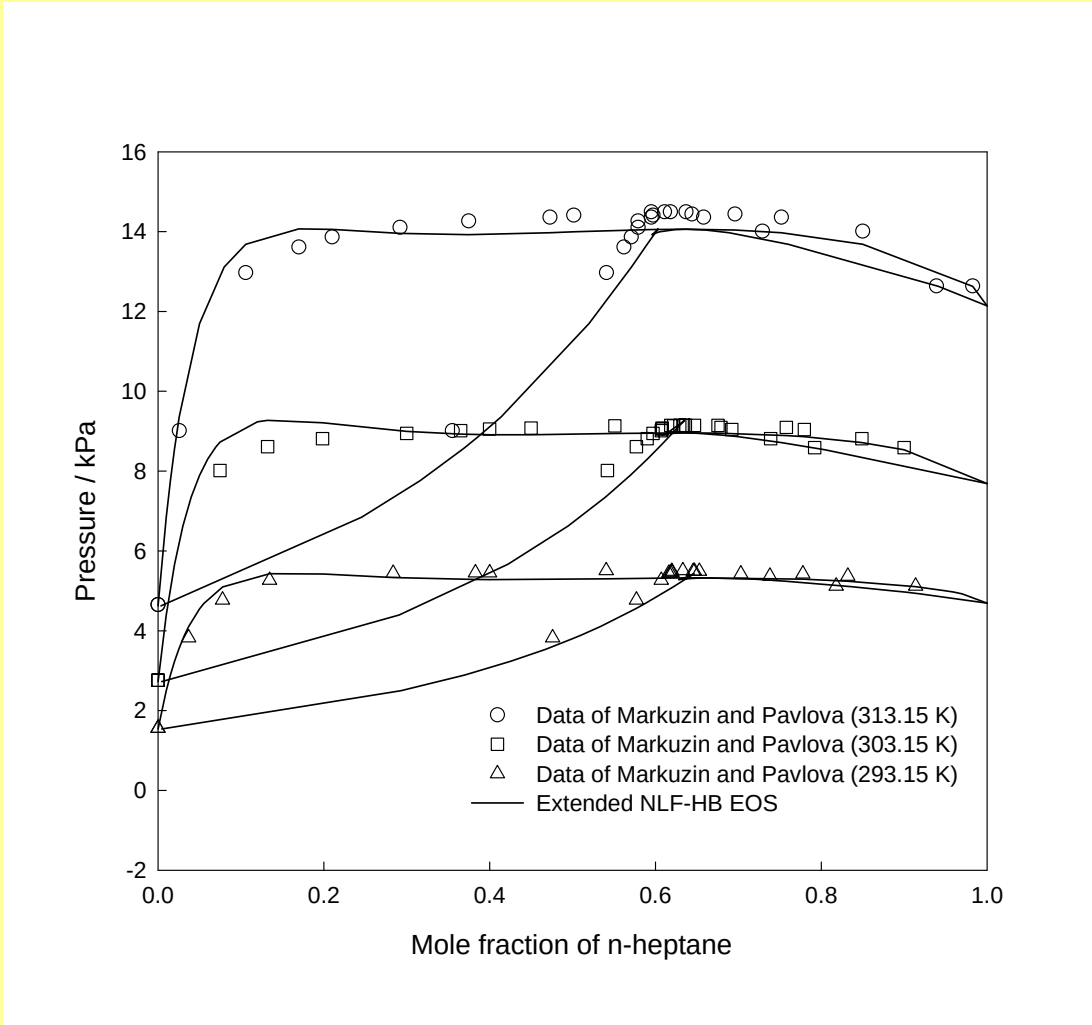


Figure. Comparison of present results with experimental data for n-heptane + acetic acid at different temperatures

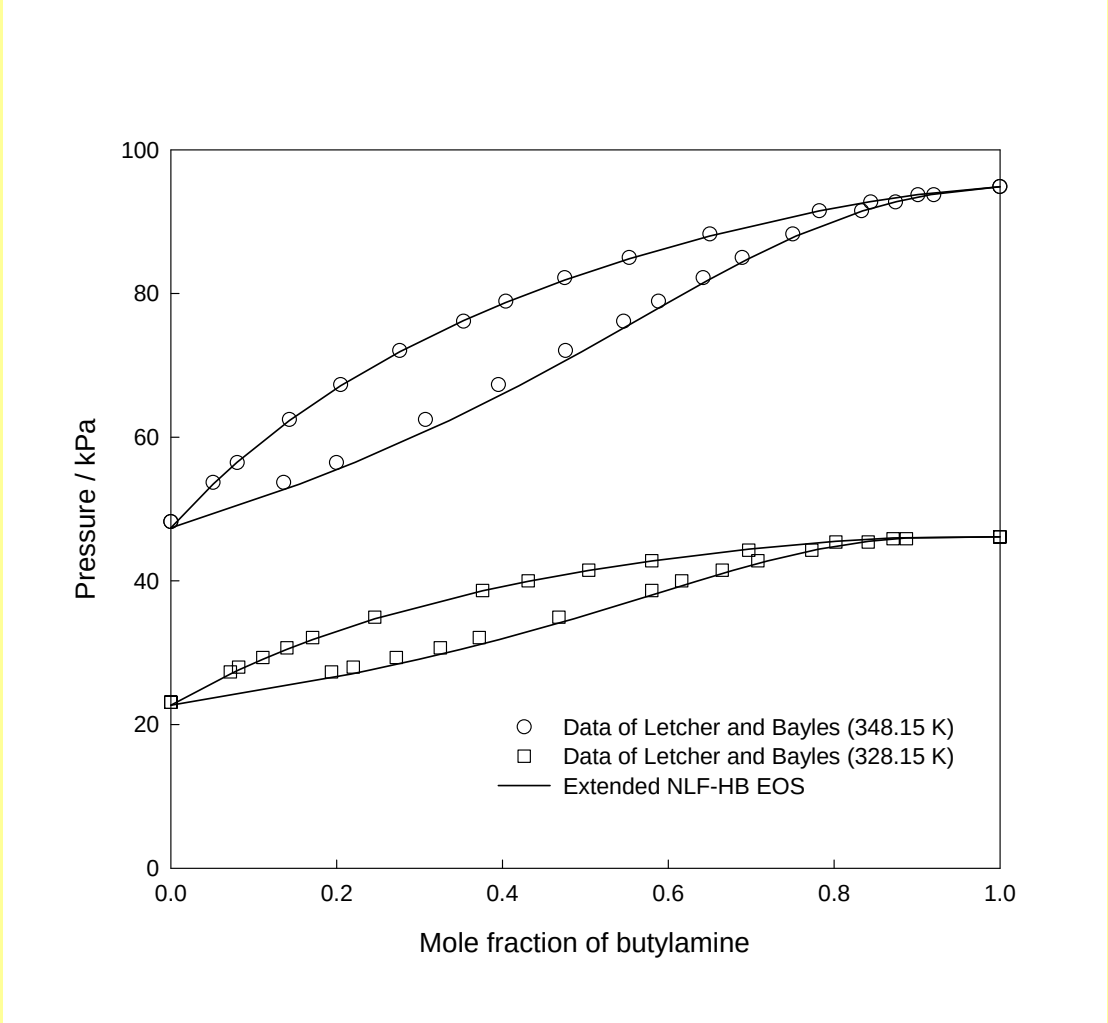


Figure. Comparison of present results with experimental data for butylamine + n-heptane at different temperatures

Conclusions

- The Veytsman statistics is extended to dimer formations
- The extended statistics is combined with the Lattice Fluid Theory of You et al.(1994) to give revised NLF-HB EOS
- The NLF-HB EOS is applied to binary mixtures of alkane, alcohol, acid, amine, and water
- Good agreements with experimental data were obtained