

Prediction of the Fluid Phase Equilibria of Binary and Ternary Mixtures



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Abstract

The objective of this work is to calculate critical and phase equilibrium properties using equations of state with mixing rules. The goal is to determine whether such equations of state models can both qualitatively and quantitatively predict the complex types of phase behaviour found in real system. The van der Waals, Guggenheim and Heilig-Franck equations are combined with the van der Waals one-fluid mixing rule and used to calculate phase equilibria of binary and ternary mixtures. Equations of state and mixing rules are also reviewed.

The unlike interaction parameters for binary mixtures of ammonia + n-alkane, ammonia + simple gases, helium + non-polar gases and water + noble gases are obtained by comparing experimental critical data with calculations using the van der Waals, Guggenheim and Heilig-Franck equations of state. These interaction parameters and equations of state are used to predict binodal curves for helium + non-polar gas and water + noble gases mixtures. The predicted binodal curves are compared with experimental data for a wide range of pressure, temperature and composition. Good agreement between theory and experiment is obtained for the isobaric temperature-composition phase behaviour and isothermal pressure-composition phenomena.

The critical properties of the carbon dioxide + ethylene + helium ternary mixture and the phase behaviour of the water + benzene + carbon dioxide ternary mixture are calculated and compared with experimental results. The purpose of the analysis is to illustrate how the calculation of ternary critical transitions and phase behaviour can provide an insight into the general fluid phase behaviour of multicomponent mixtures. The calculations are in qualitative agreement with available experimental results. Theoretical ternary mixtures of equal size components are studied.

There is considerable interest in the prediction of phase equilibria of ternary and multicomponent mixtures. This research just presents a window on the phase behaviour of ternary and multicomponent fluids. The challenge for the future is to improve our ability to predict the phase behaviour of ternary and multicomponent fluid and the most important is to accurately model multicomponent fluids.

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Declaration

I hereby declare that the thesis, entitled "Prediction of the Fluid Phase Equilibria of Binary and Ternary Mixtures" and submitted in fulfilment of the requirements for the Degree of Doctor of Philosophy in School of Information Technology of Swinburne University of Technology, is my own work and that it contains no material which has been accepted for the award to the candidate of any other degree or diploma, except where due reference is made in the text of the thesis. To the best of my knowledge and belief, it contains no material previously published or written by another person except where due reference is made in the text of the thesis.

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NOTATION

Abbreviations

APACT	associated perturbed anisotropic chain theory
BWR	Benedict-Webb-Rubin
CPA	cubic plus association
gl	gas liquid
GF-D	generalised Flory-dimer
HCB	hard convex body
HSE	hard-sphere expansion
HTA	high temperature approximation
ll	liquid liquid
lv	liquid liquid vapour
LCEP	lower critical end point
LJ-SAFT	Lennard-Jones statistical associating fluid theory
MHV1	modified Huron-Vidal first order
MHV2	modified Huron-Vidal second order
PACT	perturbed anisotropic chain theory
PHCT	perturbed hard chain theory
PR	Peng-Robinson
PVT	pressure volume temperature
RK	Redlich-Kwong
RKJZ	Redlich-Kwong-Joffe-Zudkevitch
RPA	random phase approximation
SAFT	statistical associating fluid theory
SAFT-HS	statistical associating fluid theory - hard sphere
SAFT-VR	statistical associating fluid theory - variable range
SPHCT	simplified perturbed hard chain theory
SRK	Soave-Redlich-Kwong
SSAFT	simplified statistical Associating fluid theory
STPT-D	simplified thermodynamic perturbation theory dimer
TPT	thermodynamic perturbation theory
TPT-D1	thermodynamic perturbation theory dimer 1

TPT-D2	thermodynamic perturbation theory dimer 2
TPT1	first-order thermodynamic perturbation theory
TPT2	second-order thermodynamic perturbation theory
UCEP	upper critical end point
VLE	vapour liquid equilibrium
WCA	Weeks-Chandler-Andersen
WCA-LL-GH	Weeks-Chandler-Andersen Lee-Levesque Grundke-Henderson

Latin Alphabet

a	equation of state parameter
A	Helmholtz function
b	equation of state parameter
c	equation of state parameter; 1/3 the number of external degrees of freedom
e	equation of state constant
f	conformal parameter, free energy
g	conformal parameter; interaction energy between molecules
G	Gibbs function
$g_{HS}(\mathbf{S})$	site-site correlation function
$g_0(r)$	radial distribution function
h	conformal parameter
k	Boltzmann constant; equation of state constant
k_{ij}	interaction parameter
m	number of segments; number of monomers
n	number of moles
N	number of molecules
N_A	Avogadro's number
p	pressure
\tilde{p}	reduced pressure
q	number of external segments per molecule
r	intermolecular distance; the number of segments in a molecule
R	Universal gas constant; $1/4\pi$ multiple of the mean curvature integral

S	shortest surface-to-surface distance between two molecules; number of segments per molecule
S	surface areas
T	temperature
\tilde{T}	reduced temperature
u	intermolecular potential
U(r)	potential energy
\tilde{v}	reduced volume
\tilde{v}_d	reduced volume
V	volume
V_f	free volume
W	(as defined in 4.20)
x	mole fraction
X	(as defined in 4.21)
Y	equation of state parameter
Y	parameter of SPHCT equation of state; (as defined in 4.22)
Z	compressibility

Greek Alphabet

α	non-sphericity parameter
β	equation of state parameter
ϵ	energy of interaction; depth parameter of attractive well
ζ	interaction parameter; reduced density
η	packing fraction
θ	characteristic of the equation of state
λ	equation of state parameter, width of well
μ	chemical potential
ξ	interaction parameter
π	3.14159
ρ	number density
σ	distance of interaction between molecules

τ	numerical constant
ϕ	characteristic of the equation of state
$\phi(r)$	pair potential
ω	acentric factor; orientation of molecule
Λ	length of the thermal de Broglie wave
Σ	summation

Subscripts and Superscripts

'	successive derivative; different phase
"	successive derivative; different phase
0	denotes component; reference system
1	denotes component; first-order term of perturbation theory
2	denotes component; second-order term of perturbation theory
*	configurational property; perfect gas contribution
ani	anisotropic
assoc	association
att	attractive
BH	Barker-Henderson
c	critical property
cb	combinational property
chain	chain term
dipole	dipole -dipole term
disp	dispersion
D_{ij}	universal constants
es	equivalent substitute property
HC	hard chain
hcb	hard convex bodies
hBH	hybrid Barker-Henderson
HD	hard dimer
Hs	hard sphere
HS	hard sphere

HTA	high temperature approximation
i	ith component
ideal	ideal gas
j	jth component
LJ	Lennard-Jones
m	mixture
mf	long-range dispersion forces
mono	monomer-monomer term
p	perturbation
r	rotational motion of a molecule; number of segment per molecule
rep	repulsive
RPA	random phase approximation
res	residual
R	repulsive
seg	segment
SW	square well
v	vibrational motion of a molecule
VDW	van der Waals