

Global Phase Diagrams and Critical Phenomena of Binary  
Mixtures

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## Abstract

In this work, we study the phase behaviours of binary mixtures. The main aim is to examine the global phase diagram with Guggenheim, Carnahan-Starling van der Waals and Hard Convex Body van der Waals equation of state in conjunction with van der Waals one fluid model and combining rules. Calculations of the critical properties of binary mixtures are used to determine the global phase diagram of binary mixtures.

Calculations of the critical properties of binary mixtures of components of equal size are reported using the Guggenheim equation of state. Type VI phase behaviour is predicted successfully indicating that closed-loop liquid-liquid equilibria can be obtained from hard-sphere + van der Waals interactions. Closed-loop liquid-liquid equilibria occur in the region of the global phase diagram characterized by moderately strong unlike interactions and components with very dissimilar critical temperatures. The Guggenheim equation can predict all experimentally known phase behaviour types, except type VIII. In addition, other hypothetical phase behaviour types are also predicted.

Calculations of the critical properties of binary mixtures are reported using the Carnahan-Starling-van der Waals equation of state and the Lorentz-Berthelot rules for unlike interactions. A feature of the calculations is that no unlike interaction parameters were used in the combining rules. This means that the global phase diagram can be constructed in the terms of experimentally measurable quantities such as the ratio of the critical temperatures and critical volumes of the component molecules. It is shown that most of

observed phase behaviour of binary mixtures can be obtained by simply varying the critical temperature and critical volumes of the pure components.

Calculations of the critical properties of a hypothetical binary mixtures composed of components of identical volume but different geometry as described by the  $a$  parameter are reported using hard convex body van der Waals (HCBvdW) equation of state. The  $a$  parameter of the HCBvdW equation of state have an important influence on the  $a$  and  $b$  parameters and the critical compressibility factor  $Z_c$ . Only type I, II, III and a special case of type IV phase behaviour are observed.

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## **Declaration**

I declare that the thesis, entitled “Global Phase Diagrams and Critical Phenomena of Binary Mixtures” and submitted in fulfillment 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*

ACEP	azeotropic critical end points
AZ	azeotropy
CPLP	critical pressure landing point
CPSP	critical pressure step points
CSvdW	Carnahan-Starling-van der Waals
dCPM	degenerated critical pressure maximum or minimum
DCEC	double critical end cusp
DCECP	double critical end cusp point
DCEP	double critical end points
ESTPT-D	empirical simplified thermodynamic perturbation theory-dimer
EOS	equation of state
GH	Grundke and Henderson
Gi	Ginzburg number
HCB	hard convex body
HCBC	hard convex body chain
HCBvdW	hard convex body van der Waals
HSC	hard-sphere chain
HSE	Hard-sphere expansion

LCEP	lower critical end point
LCSP	lower critical solution point
LL	Lee and Levesque; liquid liquid
LLV	liquid liquid vapour
L-S	liquid-solid
MDP	mathematical double point
PHCP	Perturbed-Hard-Chain-Theory
PTV	pressure, temperature, volume
RK	Redlick - Kwong
SAFT	statistical associating fluid theory
SPHCT	simplified perturbed hard chain theory
STPT-D	simplified thermodynamic perturbation theory-dimer
TCP	tricritical point
TPT	thermodynamic perturbation theory
TPT-D	thermodynamic perturbation theories-dimer
UCEP	upper critical end point
UCSP	upper critical saddle point
vdW	van der Waals
V-L	vapour-liquid
VL	vapour liquid
V-S	vapour-solid
WCA	Weeks-Chandler-Andersen

*Latin Alphabet*

a	equation of state parameter
A	Helmholtz function
$\tilde{A}$	reduced Helmholtz function
b	equation of state parameter
B	second virial coefficient
c	constant of degrees of freedom of a molecule for SPHCT; constant in Eq. (3.55)
C	critical point; third virial coefficient
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
I	hard sphere constant
h	conformal parameter
k	Boltzmann's constant; equation of state constant
$k_{ij}$	interaction parameter
m	m-th component; m-th segment in a chain
n	number of moles
N	number of molecules

$p$	pressure
$\tilde{p}$	reduced pressure
$q$	the number of external segments per molecule; parametric variable
$r$	intermolecular distance
$R$	universal gas constant
$S$	surface area
$T$	temperature
$\tilde{T}$	reduced temperature
$u$	intermolecular potential
$U(r)$	potential energy
$\tilde{v}$	reduced volume
$V$	volume
$W$	function of critical point
$x$	mole fraction
$X$	function of critical point
$y$	packing fraction
$Y$	parameter of SPHCT equation of state; crossover function; Condition of critical point
$Z$	compressibility factor

### *Subscripts and Superscripts*

+	positive
-	negative
*	configurational property; perfect gas contribution
`	successive derivative
``	successive derivative
0	denotes component; references system
1, 11	denotes component; first component in the mixture
2, 22	denotes component; second component in the mixture
ani	anisotropic
c	critical
cb	combinational property
es	equivalent substance
i	i-th component
iso	isotropic contribution
j	j-th component
m	mixture
p	pressure
r	ratio
T	temperature
V	volume
a	critical exponent; branch type of phase behaviour

$\beta$	critical exponent; branch type of phase behaviour
?	critical exponent; parameter in Eq. (3.67) - Eq. (3.70); branch type of phase behaviour
d	critical exponent; branch type of phase behaviour
e	branch type of phase behaviour

*Greek Alphabet*

O	equation of state parameter
a	non-sphericity parameter; constant in Eq. (3.55)
$\beta$	equation of state parameter
?	parameter from experiment
<b>e</b>	energy of interaction; reflects different in temperature from critical temperature
?	interaction parameter; reduced density
?	packing fraction; topology parameter
?	characteristic of the equation of state
?	equation of state parameter, width of well; topology parameter
$\mu$	chemical potential
?	interaction parameter
p	3.14159
?	number density
s	distance of interaction between molecules

t	numerical constant;
$f$	characteristic of the equation of state
?	acentric factor
?	length of the thermal de Broglie wave
?	summation