CHAPTER 5

DISCUSSIONS

5.1 Representation of Pure Component Properties

In order to test the accuracy and capacity of the proposed modification , a comparison between the predicted saturated properties of pure components and those of experimental values were made. The properties tested were vapor pressure, saturated vapor volume, saturated liquid volume denoted by VAP PRESS , SAT VAP VOL and SAT LIQ VOL respectively. For each property, average absolute percent deviation, AAD was calculated. The symbol AAD denoted average absolute deviation defined by

$$AAD = \frac{\sum_i |d_i|}{n}$$

where d_i is the relative percent deviation and n is the number of data points.

5.2 Saturated Liquid and Saturated Vapor Densities

Generally, saturated liquid density values calculated from the SRK equation are lower than experimental values as shown in Fiqures 4.3 to 4.12 and the PR equation predicts saturated liquid densities

which are higher at low temperatures and lower at high temperatures than the experimental values for all ten pure components. In Figures 4.3 to 4.12, the prediction of saturated liquid densities by the modified hard sphere equation agrees very well with the experimental data. The saturated vapor densities have also been compared in Figures 4.3 to 4.12 for ten pure components investigated. It can be seen that this modified hard sphere equation predicted saturated vapor densities as well as the PR and SRK equations except in the critical region.

Figures 4.13 to 4.32 show that the modified hard sphere equation predicted saturated liquid volumes as well as the hard sphere ICL equation and better than the PR and SRK equations. However, hard-sphere equations improved the prediction in the critical region. The average absolute deviations (AAD) of saturated liquid volumes are shown in Table 5.1. This table also indicates that the modified hard sphere equation of state gives smaller deviations between the calculated and the experimental values of saturated liquid volumes than the PR and SRK equations and the AAD of the saturated liquid volumes are about 0.2-1.5 %.

The deviations in the calculated values of saturated vapor volumes have also been compared in Figure 4.13 to 4.32 for ten pure components investigated. It can be seen that this modified hard sphere equation predicted saturated vapor volumes similarly as the hard sphere ICL and PR equations but better than the SRK equation. The average absolute deviations (AAD) of saturated vapor volumes are shown in Table 5.2. This table also indicates that the modified hard sphere equation of state gives slightly larger deviations than the PR equation in the calculated values of saturated vapor volume but gives

smaller deviations than the SRK equation and the AAD of saturated vapor volumes are about 0.4 - 2.3 %.

Table 5.1 Deviations between experimental and calculated saturated liquid volume.

Compound name	NO.of point	temperature range, C	AAD% OF SAT LIQ VOL				ref.
			SRK	PR	ICL	THIS WORK	
Methane	56	-183 to -91	3.80	8.74	-	0.51	(27)-(29)
Ethane	42	-133 to 28	9.32	7.20	0.93	0.62	(30)-(32)
Propane	123	-62 to 88	10.61	4.70	0.80	0.39	(34)-(37)
n-Butane	52	0 to 150	28.49	6.53	0.74	0.68	(38)-(40)
i-Butane	121	-23 to 130	12.59	5.40	0.52	0.57	(41)-(43)
n-Pentane	35	21 to 192	16.73	5.98	0.62	0.67	(44),(45)
i-Pentane	26	28 to 183	18.48	7.92	1.10	1.45	(46),(47)
n-Hexane	16	37 to 230	19.69	5.81	2.49	1.17	(48),(49)
Ethylene	28	-112 to -23	4.84	7.15	1.36	0.19	(32),(51)
Propylene	38	-78 to 88	9.97	6.12	0.47	0.95	(32),(52) (53)

Table 5.2 Deviations between experimental and calculated saturated vapor volume.

Compound name	NO. of point	temperature range, C	AAD% OF SAT VAP VOL				ref.
			SRK	PR	ICL	THIS WORK	
Methane	28	-183 to -83	1.00	0.69	3.40	1.17	(27)
Ethane	32	-106 to 22	2.91	2.55	2.21	2.29	(30),(32)
Propane	123	-62 to 88	1.86	1.10	1.22	1.28	(34)-(37)
n-Butane	57	0 to 140	2.11	0.93	1.66	1.75	(38)-(40)
i-Butane	115	-23 to 127	1.86	0.72	1.07	1.04	(41)-(43)
n-Pentane	30	25 to 177	2.21	1.25	1.27	1.34	(44),(45)
i-Pentane	17	28 to 157	2.17	0.84	1.36	1.02	(47)
n-Hexane	30	10 to 177	1.43	0.90	0.91	1.02	(49),(50)
Ethylene	28	-112 to -23	0.66	0.34	0.47	0.34	(32)
Propylene	38	4 to 82	3.61	0.81	2.23	2.30	(32),(52) (53)

5.3 Vapor Pressure

The SRK, PR and this modified hard sphere equations are designed with a view to reproduce accurately the vapor pressure of pure substances. A comparison of the predictions is presented in Table 5.3 for ten pure component light hydrocarbons. It can be seen that the average absolute deviations (AAD) are generally reduced using the PR equation (<1%). However, this modified hard sphere equation predicts vapor pressure similarly as the SRK equation (1-2 %). Figures 4.33 to 4.42 are the vapor pressure curves for ten pure component light hydrocarbons which show agreement between the calculated and experimental values. Figures 4.43 to 4.52 show percent deviations in vapor pressure for ten pure components investigated. It can be seen that the modified hard sphere equation predicted vapor pressure as well as the ICL and PR equations but more accurately than the SRK equation.

5.4 Compressibility Factor

Figures 4.53 to 4.56 show the compressibility values of the superheated vapor state for Ethane, Ethylene, Propane, and Propylene, which calculated by this modified hard sphere equation of state. It can be seen that this modified hard sphere equation predicted the compressibility factor values (Z) which generally agree very well with the experimental data at reduced pressure (P_r) less than 1 (or at pressure lower than critical pressure), but the predicted compressibility factors are lower than the experimental values for $P_r > 1$. Comparisons between the experimental compressibility factor

values and the calculated values by the SRK, PR, ICL and this modified hard sphere equations are made for Ethane, Ethylene, Propane, and Propylene as shown in Table 5.4 . This table shows that the modified hard sphere equation gives a slightly larger deviation than the hard sphere ICL equation but gives a slightly smaller deviation than the SRK and PR equations in the range of temperatures and pressures studied.

Table 5.3 Deviations between experimental and calculated vapor pressure.

Compound name	NO.of point	temperature range, C	AAD% OF VAP PRESS				ref.
			SRK	PR	ICL	THIS WORK	
Methane	23	-183 to -88	0.83	0.63	1.25	0.80	(27)
Ethane	22	-47 to 32	0.97	0.62	0.51	0.85	(30),(32)
Propane	157	-62 to 88	1.75	0.79	0.99	1.02	(34)-(37)
n-Butane	75	-0.5 to 152	1.17	0.55	1.15	1.16	(38)-(40)
i-Butane	123	-12 to 135	1.22	0.42	0.88	0.86	(41)-(43)
n-Pentane	42	25 to 196	1.57	0.80	1.48	1.53	(44),(45)
i-Pentane	28	28 to 186	1.47	0.60	1.99	1.56	(47)
n-Hexane	30	10 to 177	1.25	0.83	0.82	0.91	(49),(50)
Ethylene	28	-112 to -23	0.54	0.28	0.36	0.26	(32)
Propylene	38	4 to 82	1.73	0.49	1.11	1.16	(32),(52) (53)

Table 5.4 Deviations between experimental and calculation of compressibility factor.

Compound name	NO.of point	Pressure range, atm.	Temperature , C	|Δz|avg. SRK	PR	ICL	THIS WORK	ref.
Ethane	18	1 to 136	37.78	0.01511	0.01211	0.00929	0.01226	(30)
			54.44	0.01487	0.01351	0.00746	0.01290	
			71.11	0.01675	0.01673	0.00748	0.01404	
			87.78	0.01244	0.01374	0.00697	0.01292	
			104.44	0.01010	0.01215	0.00818	0.01153	
		total average		0.01385	0.01365	0.00788	0.01273	
Ethylene	13	15 to 110	15.00	0.00825	0.01650	0.01429	0.00842	(60)
			20.00	0.00953	0.01625	0.01509	0.00884	
			25.00	0.00833	0.01801	0.01534	0.00812	
			50.00	0.01386	0.01448	0.02515	0.01136	
			75.00	0.01671	0.01354	0.03234	0.01721	
		total average		0.01134	0.01576	0.02044	0.01079	
Propane	25	5 to 130	100.00	0.03214	0.01094	0.01699	0.02691	(35)
			125.00	0.03372	0.01499	0.01827	0.03304	
			150.00	0.03059	0.01368	0.01693	0.03022	
			200.00	0.02889	0.00931	0.00997	0.02732	
			253.22	0.02444	0.00595	0.01638	0.02169	
		total average		0.02996	0.01097	0.01571	0.02784	
Propylene	20	2 to 82	94.10	0.02036	0.01406	0.01084	0.00794	(52)
			100.00	0.02041	0.01560	0.00764	0.00715	
			125.00	0.01475	0.01344	0.00808	0.00685	
			150.00	0.01111	0.01933	0.00954	0.00904	
			200.00	0.00924	0.01104	0.00579	0.00337	
		total average		0.01517	0.01469	0.00838	0.00687	

5.5 Vapor-Liquid Equilibrium Calculations

The calculated results for four binary systems at twenty-eight isothermal conditions, summarized in Table 5.5, indicate that the modified hard sphere equation is suitable for VLE calculations. In the calculations, values of P and y are obtained from given T and x values (bubble point pressure calculations).

5.5.1 Comparisons with the experimental data

Comparisons of the calculated VLE results are made between the modified hard sphere equation and the experimental data on the following four binary systems : Ethane-Propane, Ethane-n-Butane, Ethane-iso-Butane and Propane-Propylene as shown in Figures 4.57 to 4.60 . In Figures 4.57 to 4.60 , very good overall agreement is observed at the temperature studied. In Figures 4.58 and 4.59 , the accuracy of the prediction is seen to degenerate as the critical pressure is approached. No attempts are made to continue the calculations into the critical region due to the excessive time required for convergence at these conditions. Table 5.5 indicates that the calculated bubble pressure (P) values generally agree very well with the experimental at high temperatures. The average percentage relative pressure $[(\Delta P/P)_{avg} .100\ \%]$ are all less than 3.4 % and calculated vapor compositions differ from experimental values $([\Delta y]_{avg})$ by less than 0.02 mole fraction as shown in Table 5.5. However, predictions of behavior at low temperatures are better than those at high temperatures as the critical pressure is approached as shown in Figures 4.57 to 4.60.

Table 5.5 Comparison of calculated and experimental values for four binary systems at twenty-eight Isothermal.

Systems	No. of data	Temperature K	[△p/p]av.100%	[△y]av.	Ref.
Ethane-Propane	6	255.38	0.50	0.0058	(56)
	9	283.16	0.65	0.0018	
	14	310.94	1.08	0.0059	
	14	322.05	0.82	0.0054	
	12	333.16	0.19	0.0070	
	10	344.27	0.48	0.0080	
	11	355.38	0.37	0.0073	
	10	366.49	0.32	0.0032	
Ethane-n-Butane	6	338.72	2.49	0.0151	(57)
	8	366.49	2.61	0.0201	
	5	394.27	1.43	0.0186	
Ethane-i-Butane	13	311.27	3.38	0.0053	(58)
	11	344.49	2.83	0.0116	
	10	377.44	2.48	0.0104	
	5	394.05	1.63	0.0112	
Propane-Propylene	11	230	2.38	0.0088	(59)
	11	240	2.62	0.0073	
	11	250	2.38	0.0059	
	11	260	2.31	0.0058	
	11	270	1.98	0.0010	
	11	280	1.71	0.0028	
	11	290	1.35	0.0027	
	11	300	1.07	0.0022	
	11	310	0.85	0.0017	
	11	320	0.65	0.0015	
	11	330	0.52	0.0012	
	11	340	0.47	0.0009	
	11	350	0.52	0.0010	

5.5.2 Comparisons with the PR equation

Comparisons of the calculated VLE results are made between the modified hard sphere equation and PR equation for four binary systems at twenty-eight isothermal conditions: Ethane-Propane, Ethane-n-Butane, Ethane-iso-Butane and Propylene-Propane. The calculated results of these two methods for four binary systems are presented in Table 5.6. It can be seen that the prediction of bubble pressure and vapor compositions by this modified hard sphere and PR equations agree very well with the experimental data. However, the modified hard sphere equation gives smaller overall average deviations between the calculated and the experimental values than the PR equation.

Table 5.6 Bubble Point Deviation for four binary system, Comparison between the PR and modified hard-sphere EOS.

Systems	NO.of points	Temperature K	[ΔP/P]avg.100% PR	[ΔP/P]avg.100% THIS WORK	[Δy]av. PR	[Δy]av. THIS WORK
Ethane-Propane	6	255.38	0.86	0.50	0.0068	0.0058
	9	283.16	0.91	0.65	0.0025	0.0018
	14	310.94	0.77	1.08	0.0048	0.0059
	14	322.05	0.60	0.82	0.0093	0.0054
	12	333.16	0.47	0.19	0.0132	0.0070
	10	344.27	0.48	0.48	0.0184	0.0080
	11	355.38	0.30	0.37	0.0141	0.0073
	10	366.49	0.26	0.32	0.0088	0.0032
	overall average		0.58	0.55	0.0097	0.0055
Ethane-n-Butane	6	338.72	3.12	2.49	0.0402	0.0151
	8	366.49	3.16	2.61	0.0707	0.0201
	5	394.27	1.02	1.43	0.0850	0.0186
	overall average		2.43	2.19	0.0653	0.0179
Ethane-iso-Butane	13	311.27	2.15	3.38	0.0073	0.0053
	11	344.49	1.99	2.83	0.0220	0.0116
	10	377.44	1.51	2.48	0.0270	0.0104
	5	394.05	1.58	1.63	0.0353	0.0112
	overall average		1.81	2.58	0.0229	0.0096
Propylene-Propane	11	230	2.77	2.38	0.0094	0.0088
	11	240	3.05	2.62	0.0077	0.0073
	11	250	2.55	2.38	0.0063	0.0059
	11	260	2.31	2.31	0.0052	0.0058
	11	270	2.06	1.98	0.0044	0.0010
	11	280	1.78	1.71	0.0035	0.0028
	11	290	1.45	1.35	0.0028	0.0027
	11	300	1.15	1.07	0.0023	0.0022
	11	310	0.88	0.85	0.0029	0.0017
	11	320	0.65	0.65	0.0016	0.0015
	11	330	0.36	0.52	0.0013	0.0012
	11	340	0.32	0.47	0.0011	0.0009
	11	350	0.25	0.52	0.0011	0.0010
	overall average		1.51	1.44	0.0038	0.0033