CHAPTER 4

RESULTS OF CALCULATIONS

4.1 The Temperature-Dependence Parameters

Based on the modified hard sphere equation of state (Equation 3.5) and the procedure in Figure 3.1 with the use of saturated liquid volume data, the temperature-dependent parameters Ω_a and Ω_b are evaluated for pure components, Methane, Ethane, Propane, n-Butane, iso-Butane, n-Pentane, iso-Pentane, n-Hexane, Ethylene and Propylene. Numerical values of the parameters obtained together with the reduced temperature ranges investigated are reported in Table 4.1. The temperature dependent characteristics of Ω_a and Ω_b demonstated in Figure 4.1 for components; Methane, Ethane, Propane, Ethylene, and Propylene, and Figure 4.2 for components; n-Butane, iso-Butane, n-Pentane, iso-Pentane, and n-Hexane.

The values of the parameters obtained above were first of all correlated in terms of reduced temperature (T_r) for all the pure components and were further correlated by means of Equations (3.9) and (3.10). The coefficients a_i and b_i were determined using the method of least-squares and are reported in Table 4.2 for the ten pure components investigated. These values were used in the calculations of this study.

Table 4.1 Numerical values of the parameters Ωa and Ωb calculated by the modified hard sphere equation.

COMPOUND NAME														
METHANE			ETHANE			PROPANE			n-BUTANE			iso-BUTANE		
Tr	Ωa	Ωb	Tr	Ωa	Ωb	Tr	Ωa	Ωb	Tr	Ωa	Ωb	Tr	Ωa	Ωb
0.60282	0.64840	0.13946	0.62213	0.65702	0.13497	0.63952	0.65870	0.13216	0.65858	0.65570	0.13007	0.63705	0.67097	0.13275
0.62903	0.63417	0.13741	0.65488	0.63685	0.13261	0.64853	0.65314	0.13154	0.70562	0.62388	0.12672	0.65175	0.66068	0.13170
0.65524	0.62067	0.13544	0.68762	0.61719	0.13017	0.65754	0.64791	0.13099	0.72914	0.60835	0.12498	0.67135	0.64767	0.13039
0.68145	0.60658	0.13321	0.70653	0.60461	0.12833	0.66656	0.64197	0.13032	0.75266	0.59302	0.12316	0.70566	0.62493	0.12792
0.70766	0.59200	0.13074	0.72037	0.59770	0.12755	0.67858	0.63433	0.12945	0.77618	0.57761	0.12121	0.73016	0.60862	0.12599
0.73387	0.57788	0.12829	0.73183	0.58861	0.12598	0.69060	0.62657	0.12853	0.82322	0.54718	0.11708	0.76446	0.58648	0.12325
0.76008	0.56490	0.12604	0.75311	0.57864	0.12482	0.73867	0.59642	0.12487	0.84674	0.53222	0.11492	0.80367	0.56125	0.11986
0.78629	0.55110	0.12346	0.75470	0.57626	0.12429	0.75970	0.58301	0.12313	0.89378	0.50261	0.11035	0.83797	0.53962	0.11675
0.81250	0.53791	0.12095	0.78979	0.55644	0.12127	0.78073	0.56967	0.12130	0.94082	0.47383	0.10566	0.85757	0.52743	0.11491
0.83871	0.52493	0.11841	0.81362	0.54284	0.11905	0.82881	0.54006	0.11711	0.95258	0.46702	0.10453	0.87227	0.51826	0.11348
0.86492	0.51229	0.11591	0.83986	0.52839	0.11663	0.84984	0.52603	0.11481	0.96905	0.45824	0.10317	0.88697	0.50922	0.11204
0.89113	0.49939	0.11326	0.87889	0.50750	0.11302	0.87087	0.51277	0.11264	0.97375	0.45584	0.10282	0.90167	0.50033	0.11061
0.91734	0.48727	0.11079	0.88409	0.50557	0.11278	0.89491	0.49737	0.10996	0.97846	0.45383	0.10258	0.91637	0.49138	0.10912
0.94354	0.47506	0.10828	0.90982	0.49029	0.10983	0.92496	0.48052	0.10710	0.98786	0.45091	0.10244	0.94088	0.47690	0.10667
0.96975	0.46365	0.10599	0.95853	0.46550	0.10534	0.95801	0.46455	0.10451	0.99022	0.45044	0.10250	0.95068	0.47135	0.10578
0.99596	0.45930	0.10601	0.98797	0.45416	0.10372	0.99106	0.45387	0.10334	0.99492	0.45087	0.10303	0.96048	0.46590	0.10488

Table 4.1 Numerical values of the parameters Ωa and Ωb calculated by the modified hard sphere equation. (Continued)

COMPOUND NAME														
n-PENTANE			iso-PENTANE			n-HEXANE			ETHYLENE			PROPYLENE		
Tr	Ωa	Ωb	Tr	Ωa	Ωb	Tr	Ωa	Ωb	Tr	Ωa	Ωb	Tr	Ωa	Ωb
0.65834	0.66273	0.12814	0.65385	0.66812	0.13049	0.67691	0.64528	0.12331	0.62326	0.64938	0.13408	0.63441	0.66045	0.13318
0.68136	0.64637	0.12664	0.67334	0.65442	0.12923	0.67850	0.64284	0.12298	0.63336	0.64339	0.13338	0.64578	0.65307	0.13242
0.72394	0.61661	0.12366	0.71678	0.62314	0.12598	0.71135	0.61879	0.12081	0.63884	0.64031	0.13304	0.64838	0.65120	0.13220
0.74524	0.60184	0.12206	0.76023	0.59309	0.12254	0.73544	0.60296	0.11941	0.65071	0.63349	0.13224	0.65414	0.64741	0.13178
0.76653	0.58749	0.12045	0.73850	0.60805	0.12430	0.74419	0.59570	0.11857	0.64560	0.63123	0.13197	0.66729	0.63881	0.13083
0.78782	0.57301	0.11873	0.80367	0.56389	0.11883	0.77704	0.57265	0.11609	0.66965	0.62241	0.13087	0.67208	0.63565	0.13046
0.80911	0.55861	0.11693	0.84711	0.53535	0.11487	0.80989	0.55029	0.11353	0.70453	0.60198	0.12816	0.68564	0.62709	0.12950
0.85170	0.53000	0.11309	0.89055	0.50737	0.11069	0.84274	0.52800	0.11073	0.72135	0.59215	0.12677	0.70551	0.61430	0.12795
0.89428	0.50177	0.10900	0.93399	0.47991	0.10635	0.87558	0.50606	0.10778	0.72592	0.59097	0.12672	0.74838	0.58729	0.12445
0.93687	0.47420	0.10476	0.95571	0.46666	0.10425	0.90843	0.48436	0.10467	0.77904	0.56094	0.12222	0.80044	0.55546	0.11990
0.97945	0.44995	0.10124	0.97743	0.45453	0.10247	0.93252	0.47139	0.10303	0.83125	0.53153	0.11740	0.88537	0.49702	0.10922
0.99862	0.45058	0.10328	0.99915	0.45423	0.10451	0.99164	0.44077	0.09948	0.88527	0.50426	0.11276	0.99496	0.46271	0.10642

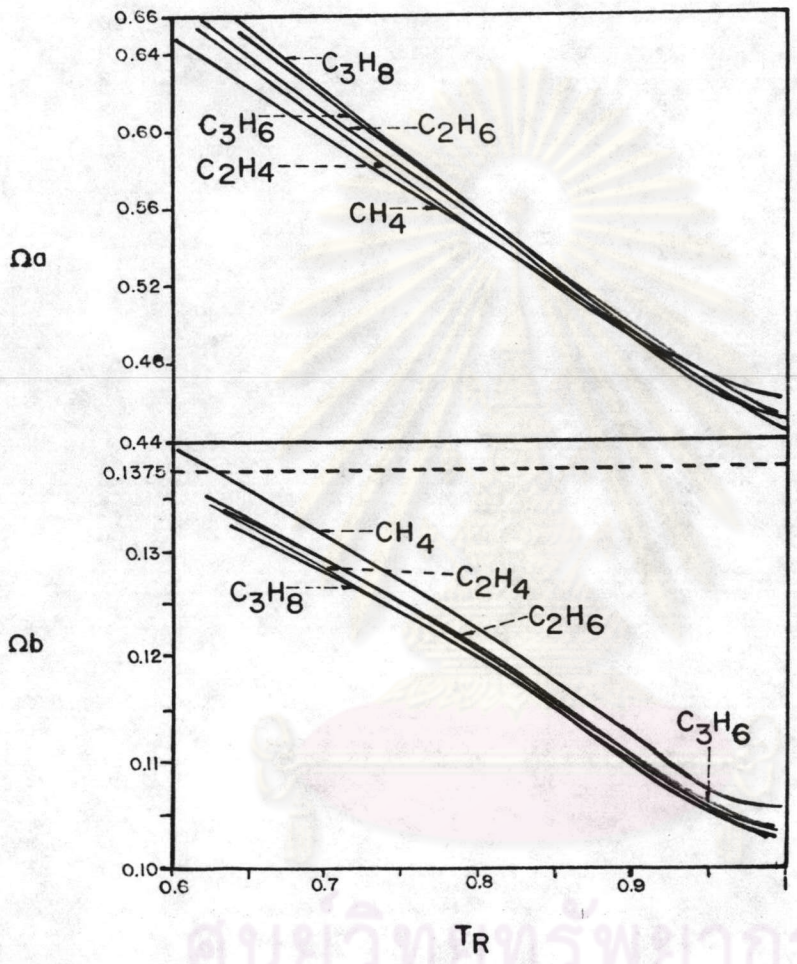

Figure 4.1 Temperature dependent characteristics of Ωa and Ωb.

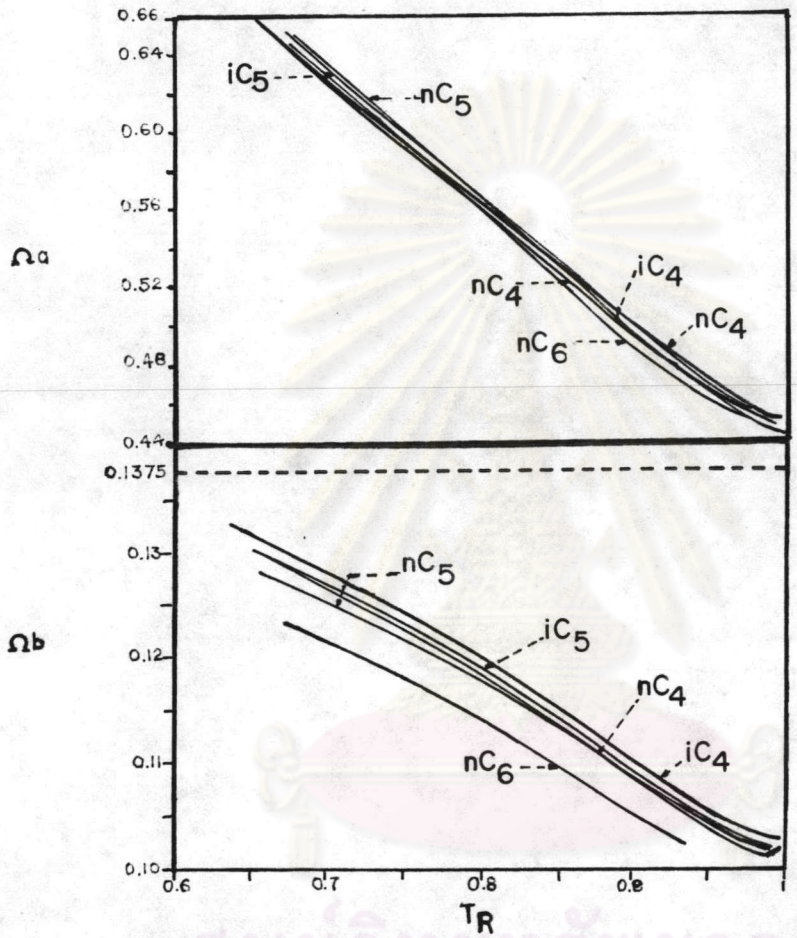

Figure 4.2 Temparature dependent characteristic of Ωa and Ωb

Table 4.2 Values of the Coefficients ai and bi of Equations (3.9) & (3.10) Determined by the Least-Squares Method.

Compound	a0	a1	a2	b0	b1	b2	Ref
Methane	1.04380	-0.75462	0.16309	0.18585	-0.06844	-0.01386	(27)-(29)
Ethane	1.09937	-0.80583	0.15014	0.16815	-0.03119	-0.03572	(30)-(32)
Propane	1.17600	-0.92966	0.19417	0.16393	-0.02232	-0.04179	(34)-(37)
n-Butane	1.24711	-1.07634	0.27110	0.17528	-0.05610	-0.01871	(38)-(40)
i-Butane	1.19469	-0.94570	0.19545	0.16297	-0.02110	-0.04071	(41)-(43)
n-Pentane	1.30387	-1.18167	0.31916	0.16750	-0.04359	-0.02365	(44),(45)
i-Pentane	1.32030	-1.22137	0.34654	0.19044	-0.09369	0.00487	(46),(47)
n-Hexane	1.40620	-1.47839	0.52176	0.18191	-0.09639	0.01466	(48),(49)
Ethylene	1.08226	-0.78977	0.15419	0.15934	-0.01065	-0.04755	(32),(51)
Propylene	1.23817	-1.11628	0.32761	0.19310	-0.09868	0.00819	(32),(52),(53)

4.2 Saturated Liquid and Saturated Vapor Densities

The saturated liquid and vapor densities for ten pure component light hydrocarbons as shown in Figure 4.3 to 4.12 were calculated by the Soave-Redlich-Kwong (SRK), Peng-Robinson (PR), and this modified hard - sphere equation (Equation (3.5)). Numerical values of the saturated liquid and vapor densities are reported in Appendix B. These values were calculated by a program called " DENSITY " of Appendix A.

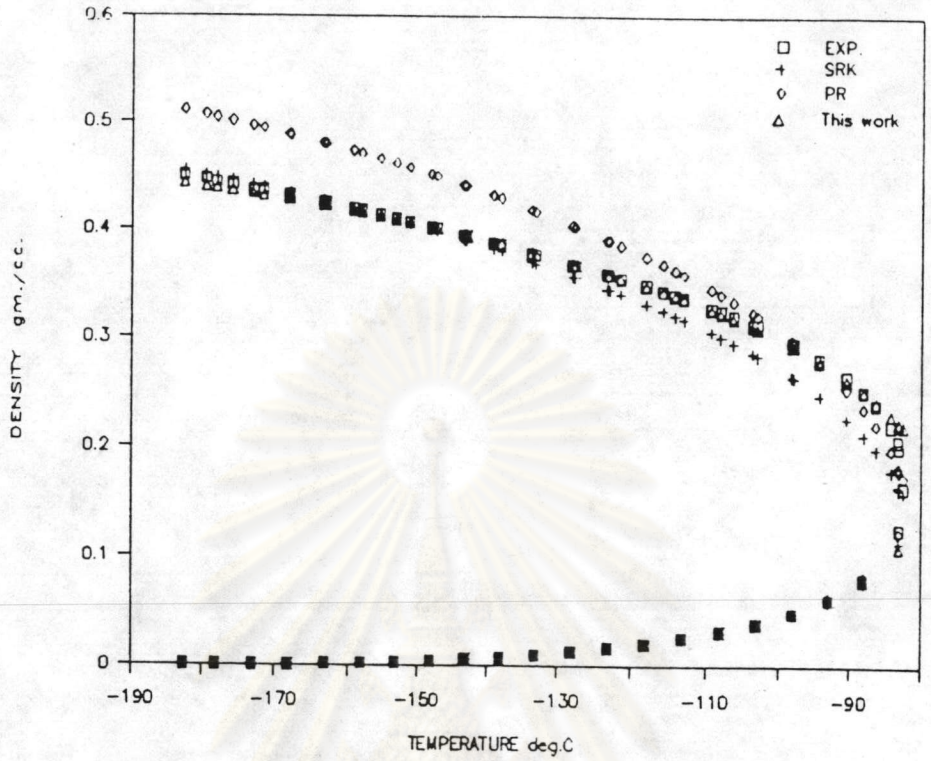

Figure 4.3 Saturated Liquid and Vapor Densities of Methane

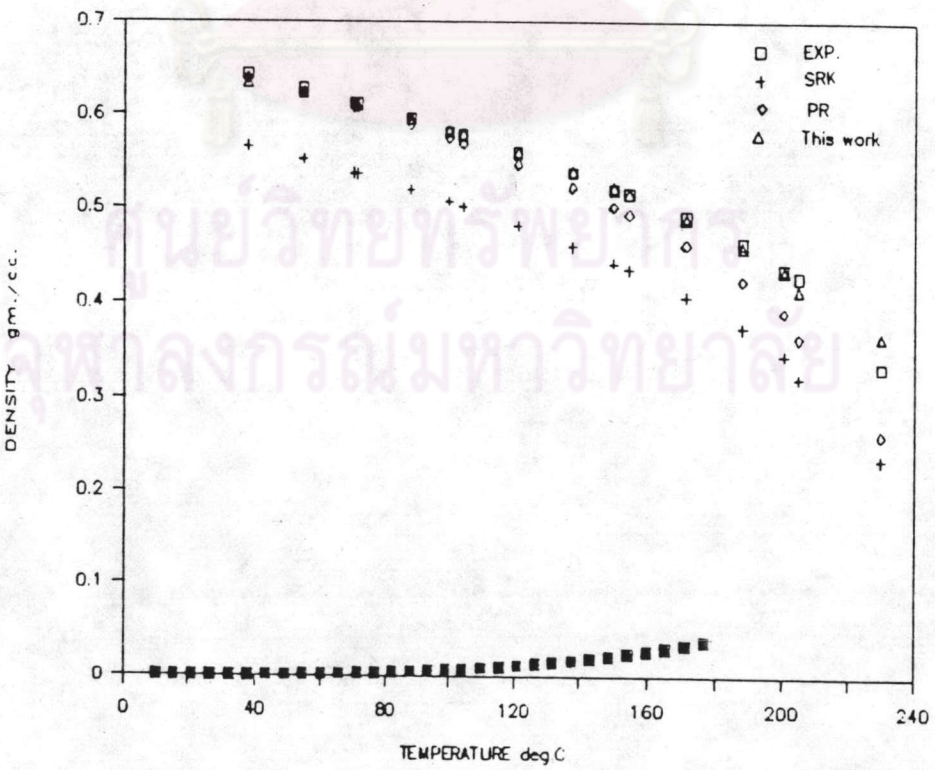

Figure 4.4 Saturated Liquid and Vapor Densities of n-Hexane.

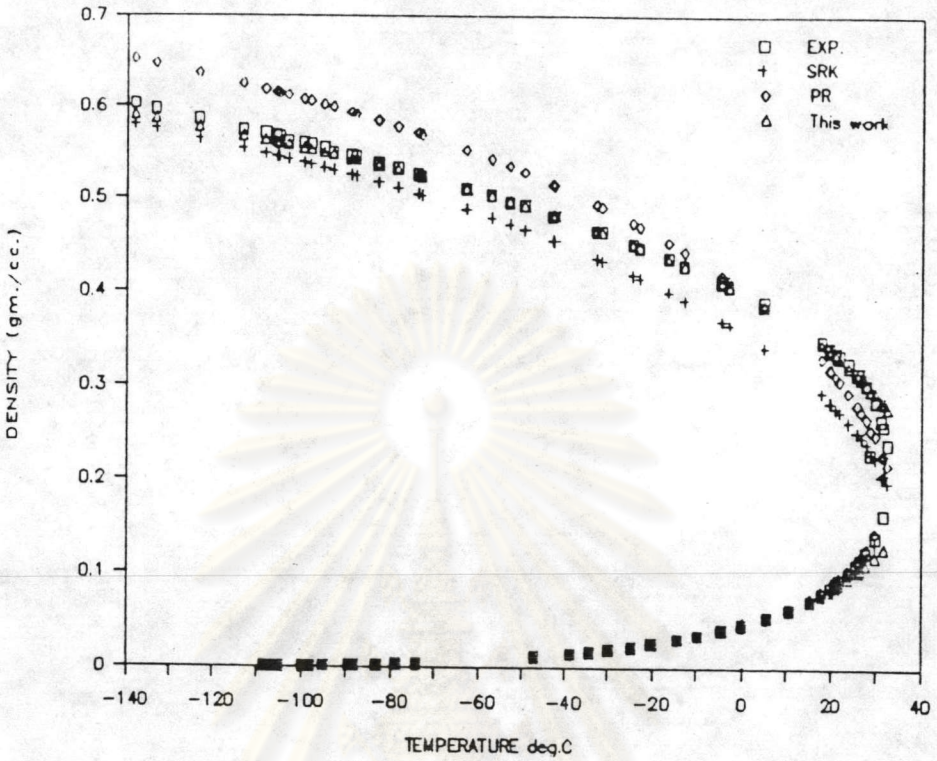

Figure 4.5 Saturated Liquid and Vapor Densities of Ethane.

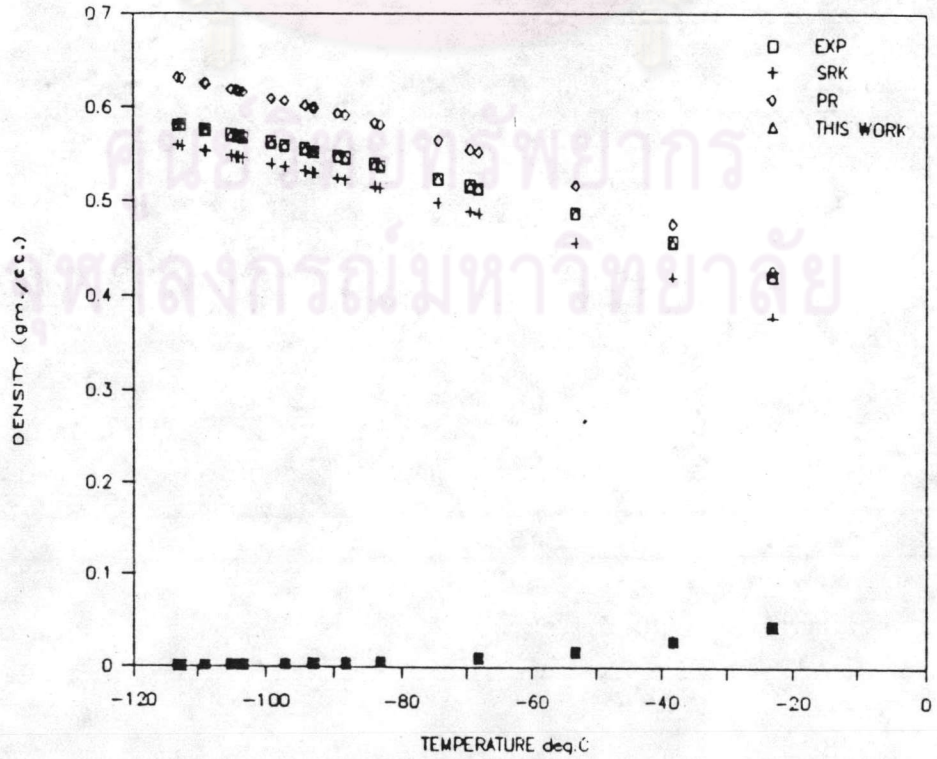

Figure 4.6 Saturated Liquid and Vapor Densities of Ethylene.

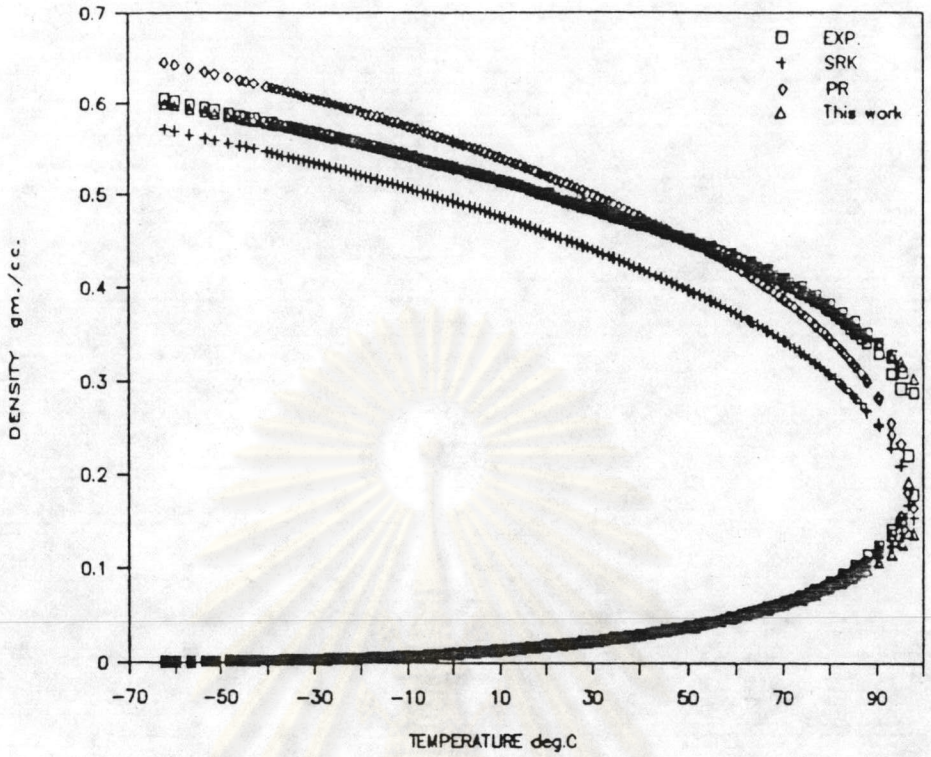

Figure 4.7 Saturated Liquid and Vapor Densities of Propane.

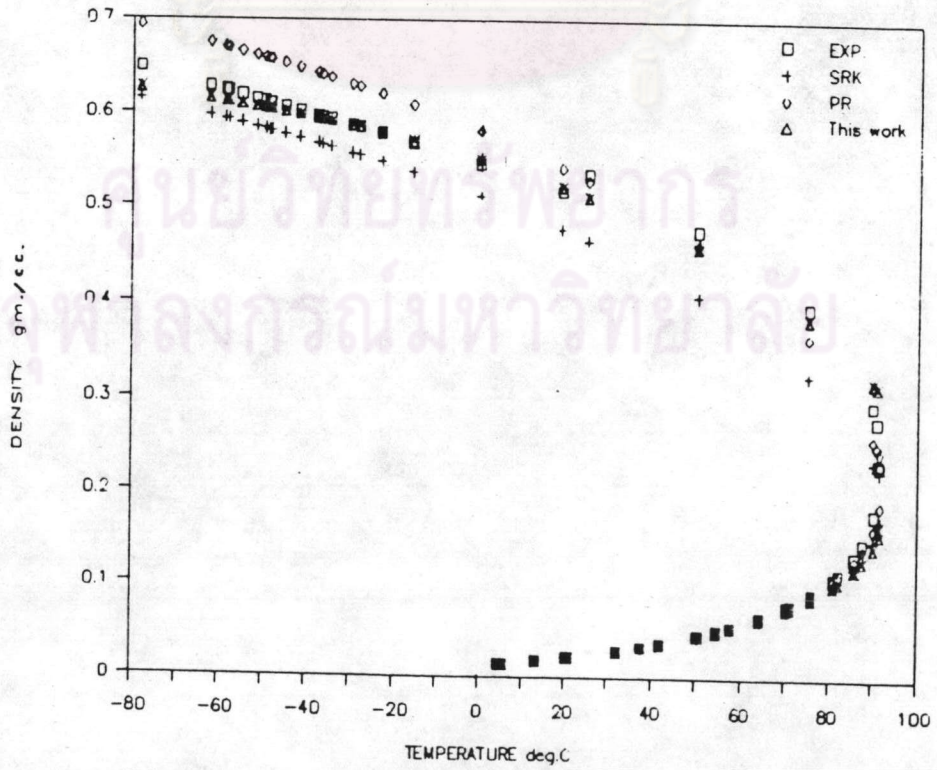

Figure 4.8 Saturated Liquid and Vapor Densities of Propylene.

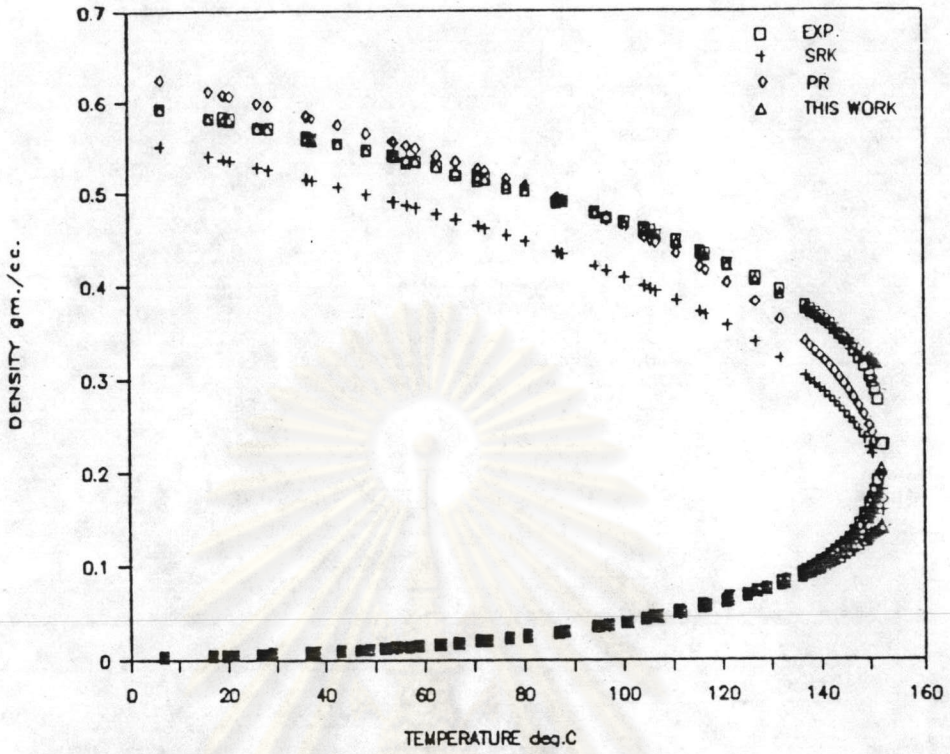

Figure 4.9 Saturated Liquid and Vapor Densities of n-Butane.

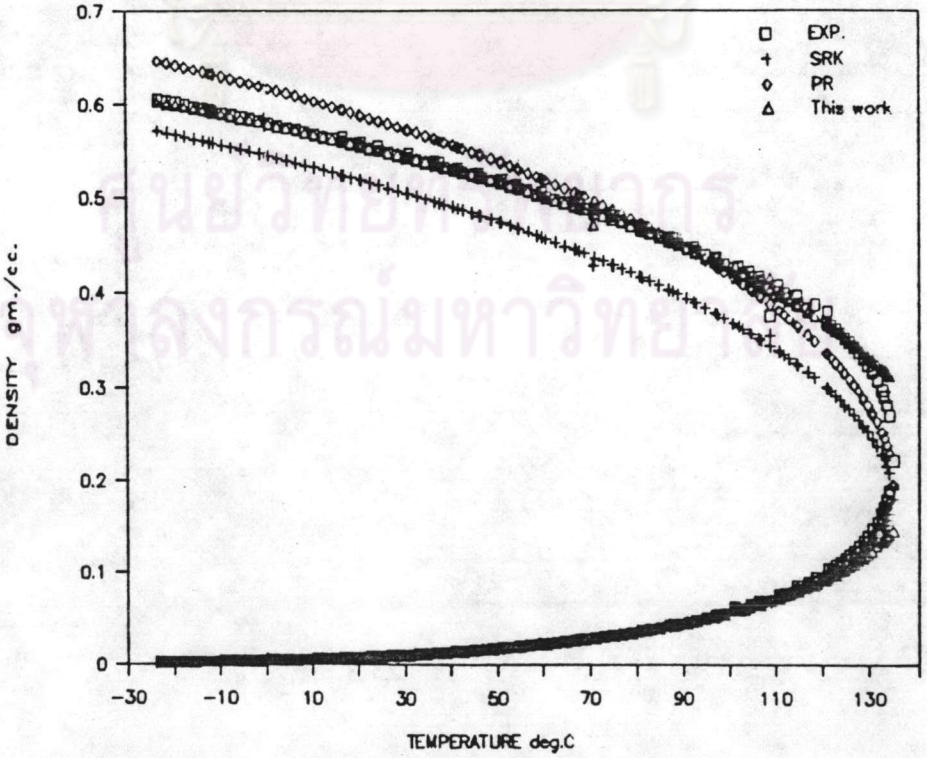

Figure 4.10 Saturated Liquid and Vapor Densities of iso-Butane.

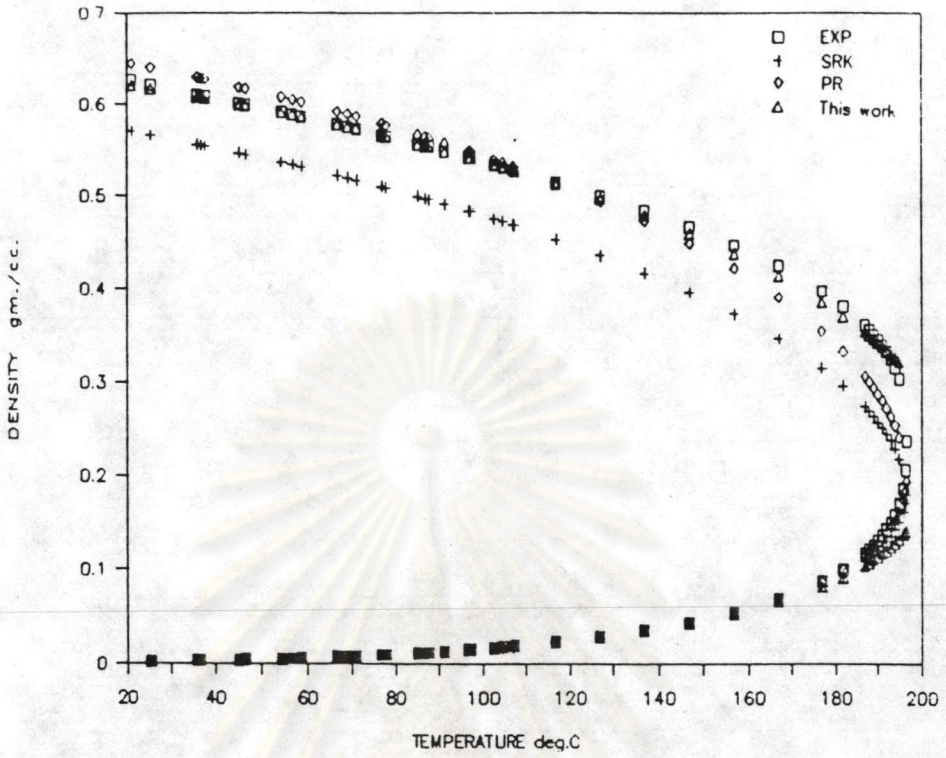

Figure 4.11 Saturated Liquid and Vapor Densities of n-Pentane.

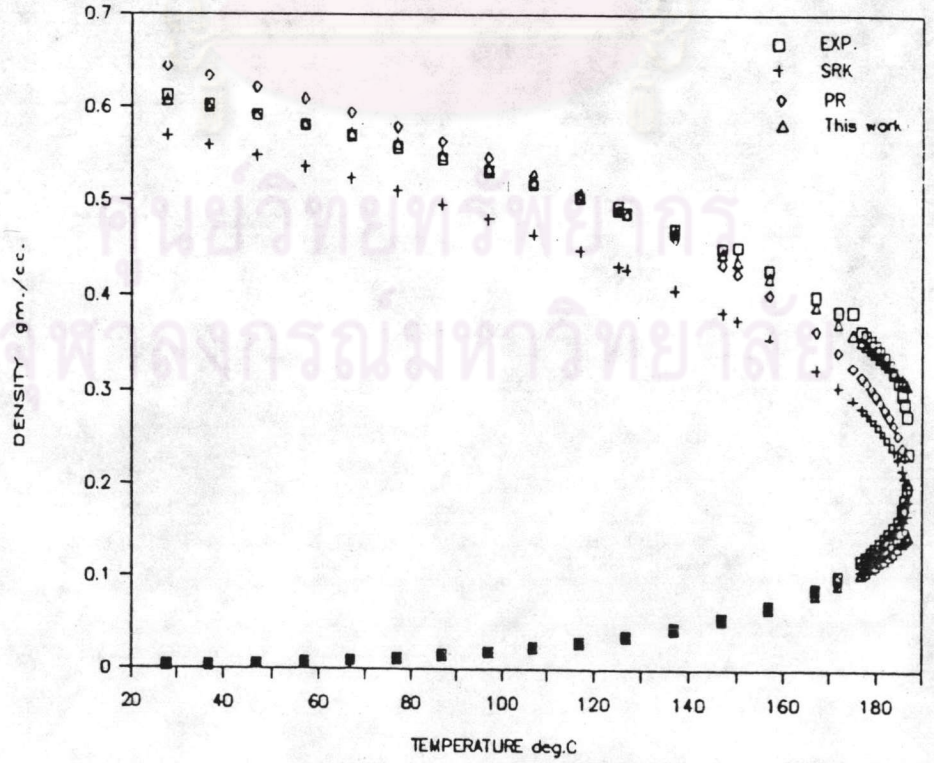

Figure 4.12 Saturated Liquid and Vapor Densities of iso-Pentane.

Figures 4.13 to 4.32 show percent deviations in saturated liquid and vapor volume for ten pure component light hydrocarbons as a function of reduced temperature, which were calculated by SRK, PR, ICL hard-sphere equations and this work (Equation (3.5)). The calculated results obtained from the SRK, PR, and ICL hard sphere are included in these figures for the purpose of comparison.

% deviation (d_i) define as :

$$\% \text{ deviation} = \frac{(V_{exp} - V_{cal})}{V_{exp}} \cdot 100$$

where V_{exp} = experimental saturated molar volume

V_{cal} = calculated saturated molar volume

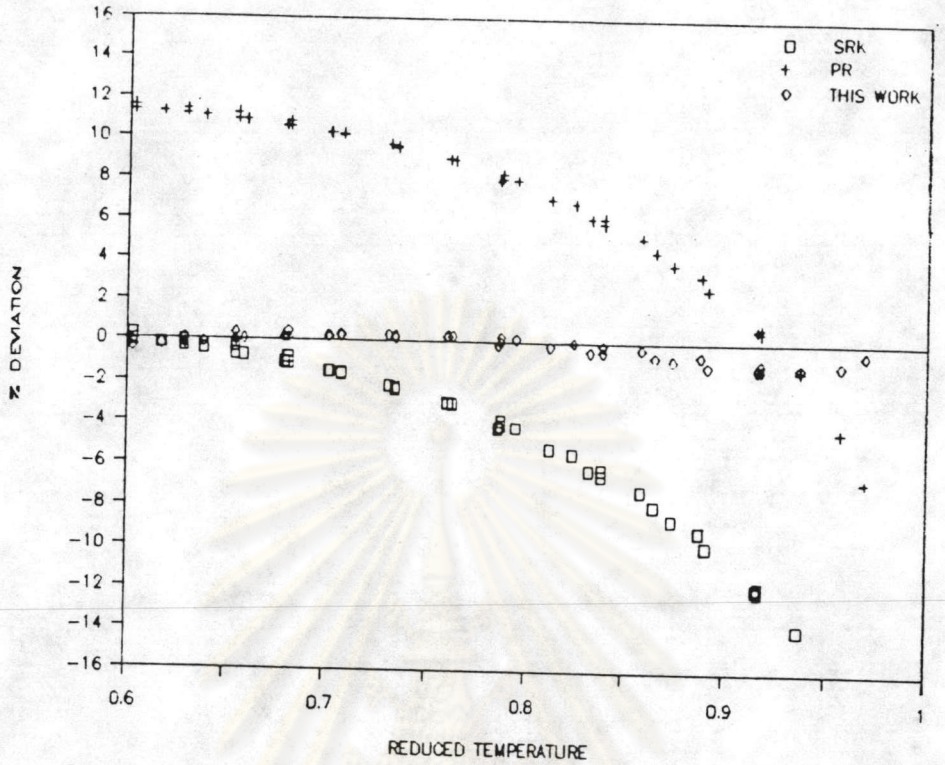

Figure 4.13 % Deviation in Saturated Liquid Volume for Methane

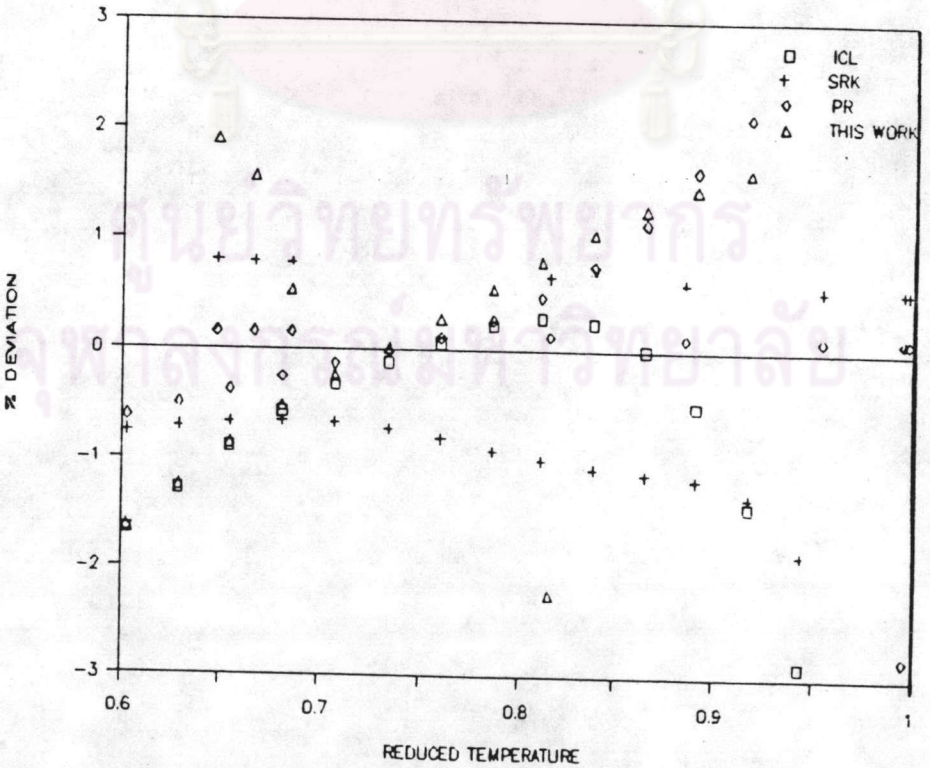

Figure 4.14 % Deviation in Saturated Vapor Volume for Methane

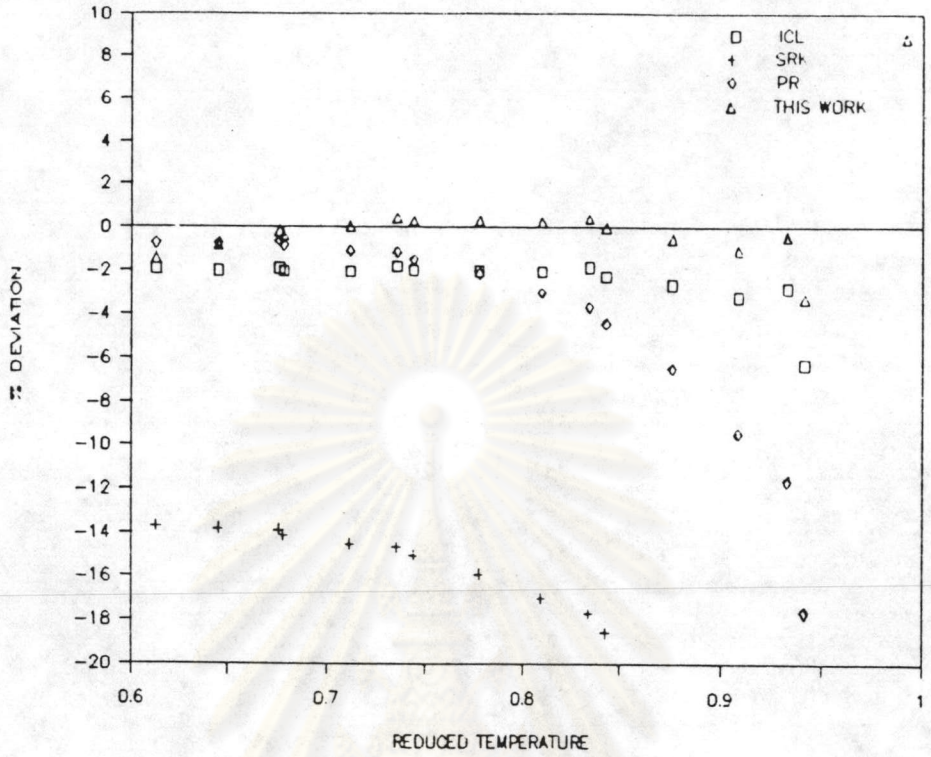

Figure 4.15 % Deviation in Saturated Liquid Volume for n-Hexane

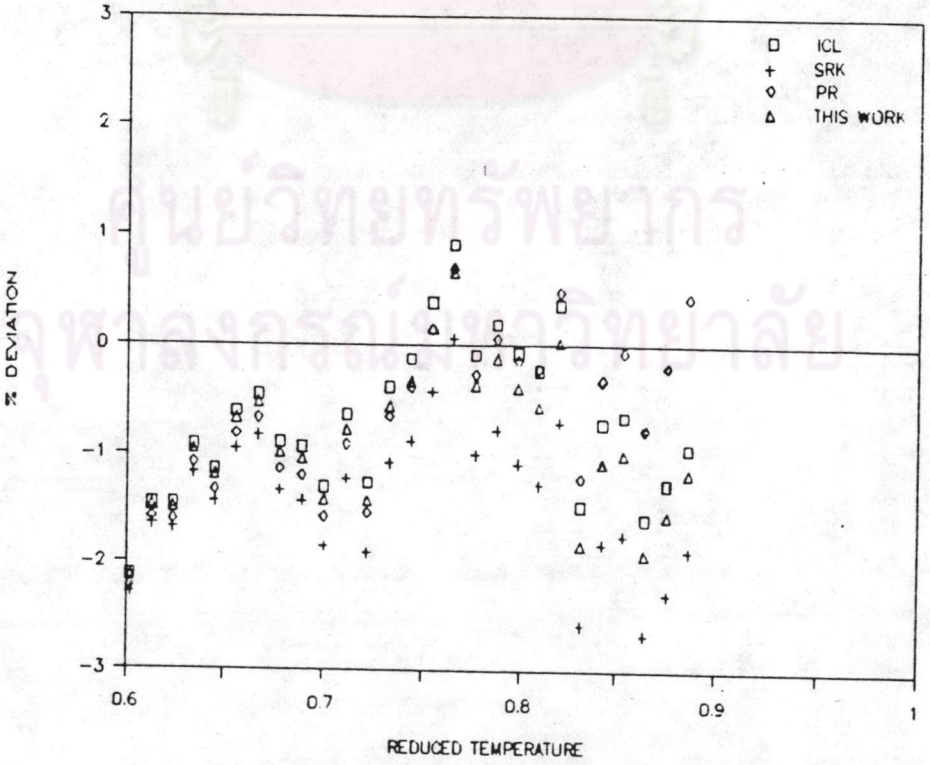

Figure 4.16 % Deviation in Saturated Vapor Volume for n-Hexane

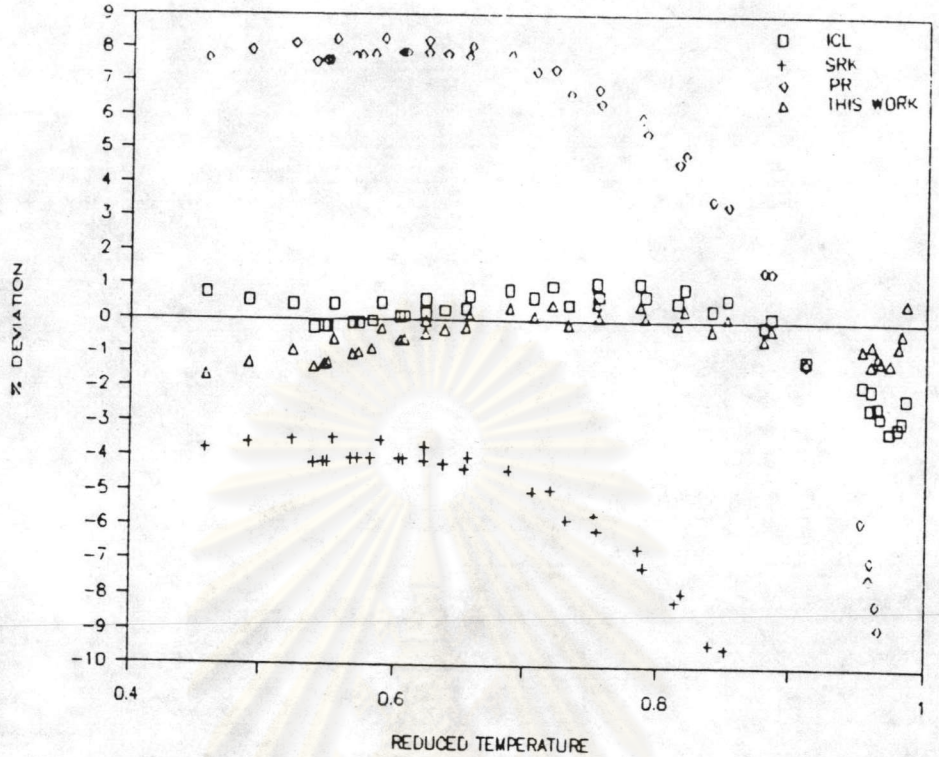

Figure 4.17 % Deviation in Saturated Liquid Volume for Ethane

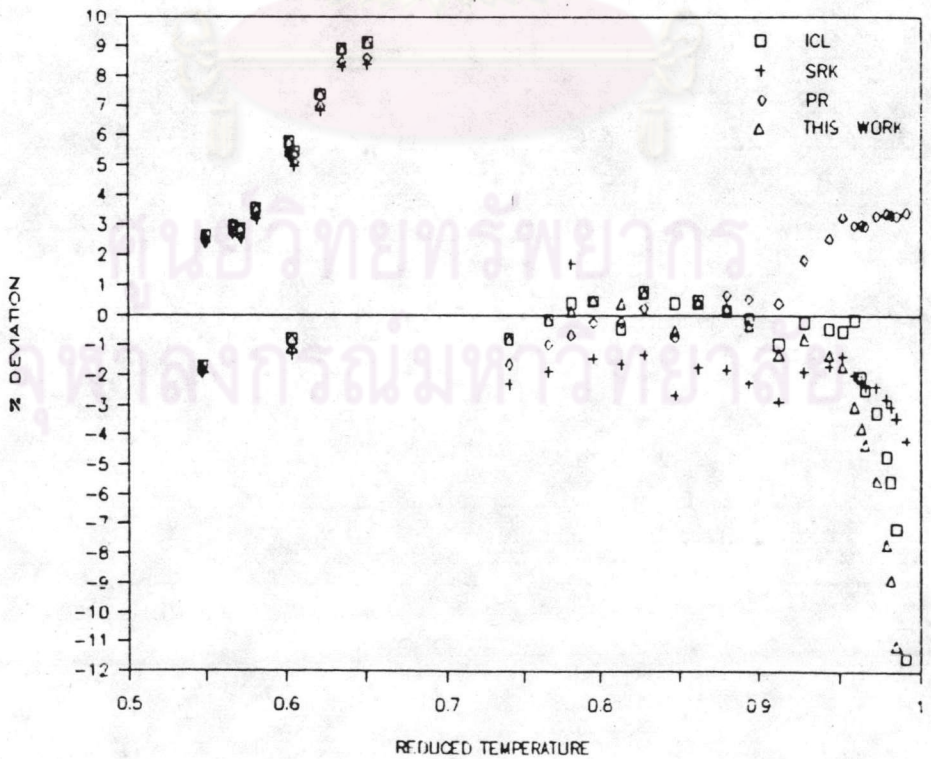

Figure 4.18 % Deviation in Saturated Vapor Volume for Ethane

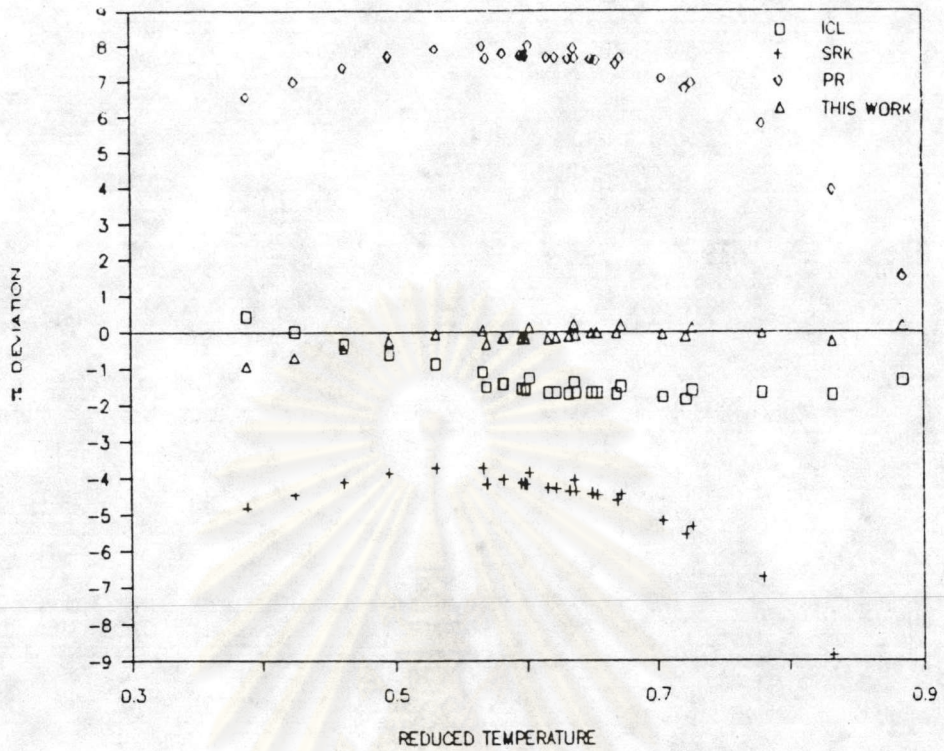

Figure 4.19 % Deviation in Saturated Liquid Volume for Ethylene

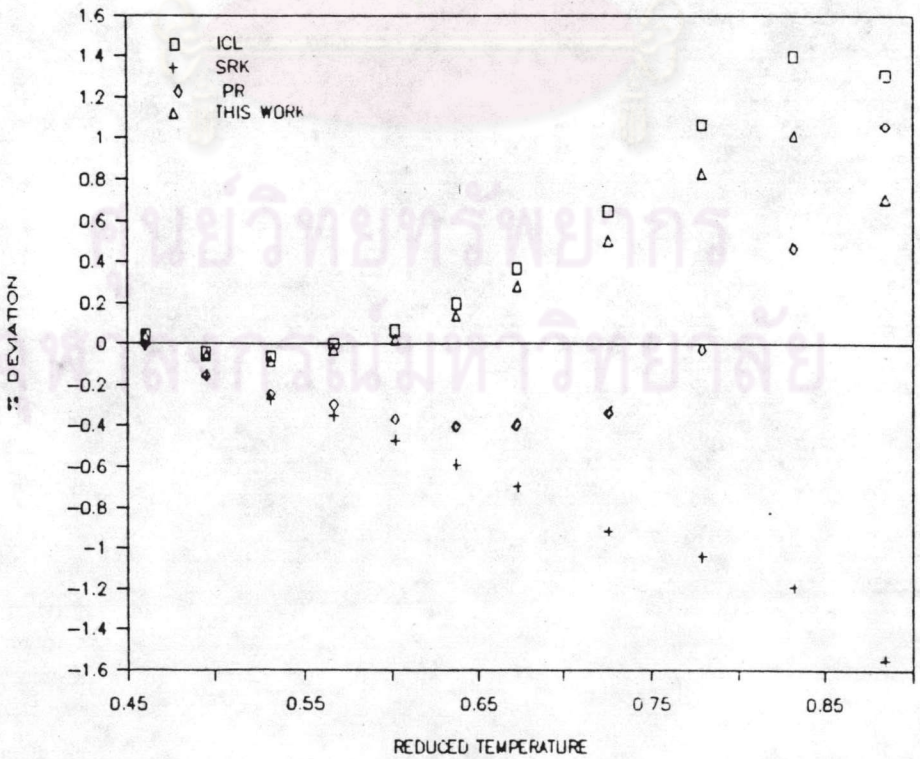

Figure 4.20 % Deviation in Saturated Vapor Volume for Ethylene

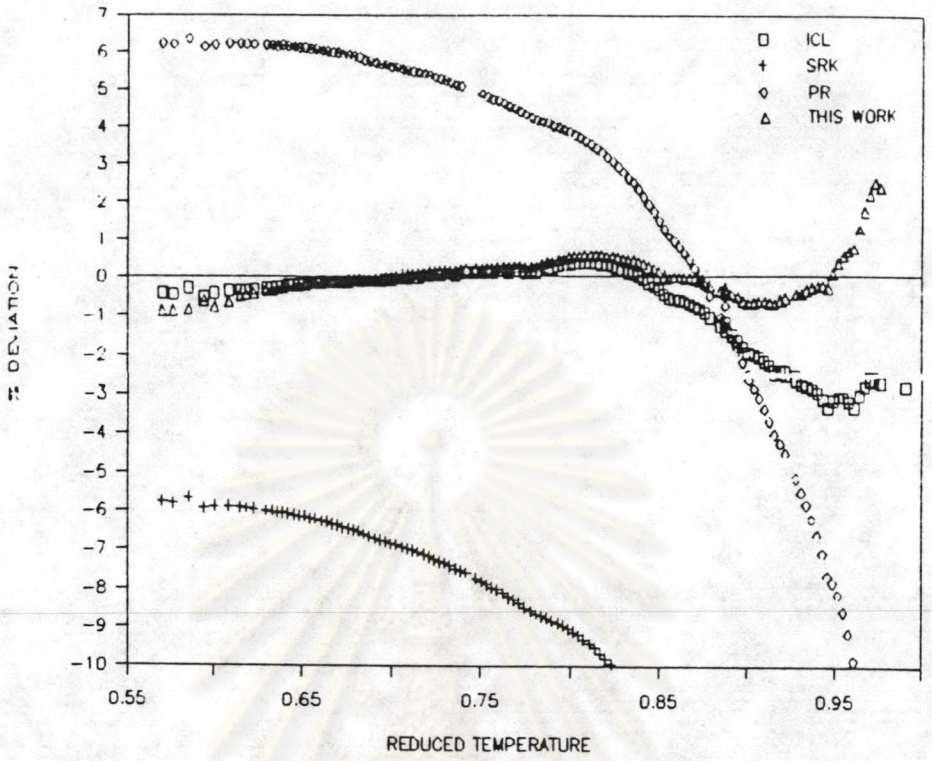

Figure 4.21 % Deviation in Saturated Liquid Volume for Propane

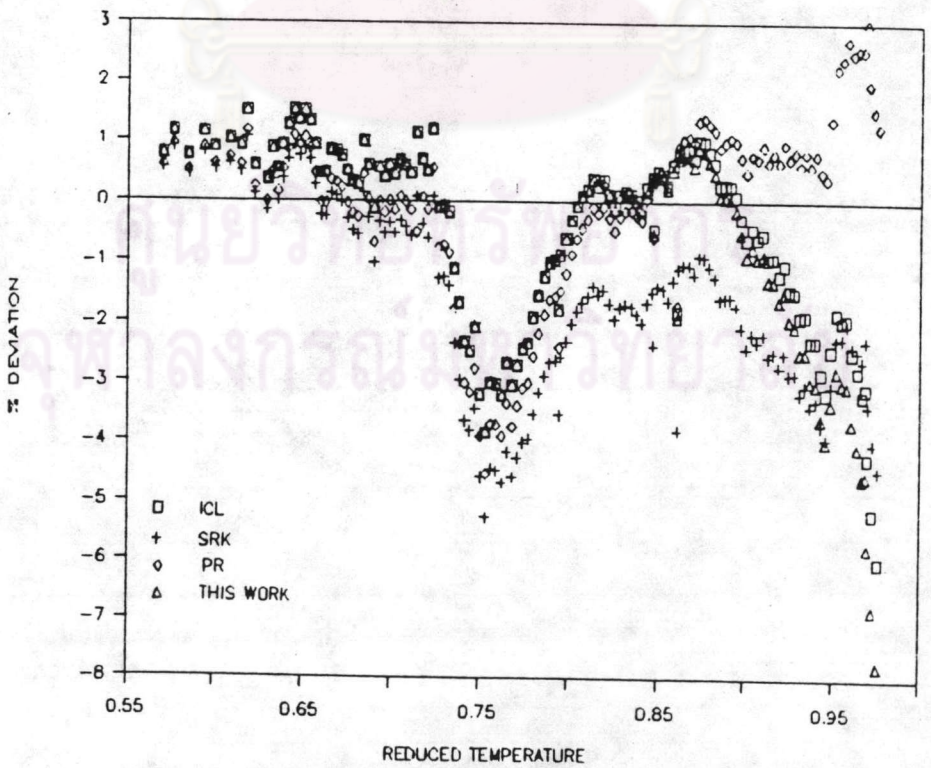

Figure 4.22 % Deviation in Saturated Vapor Volume for Propane

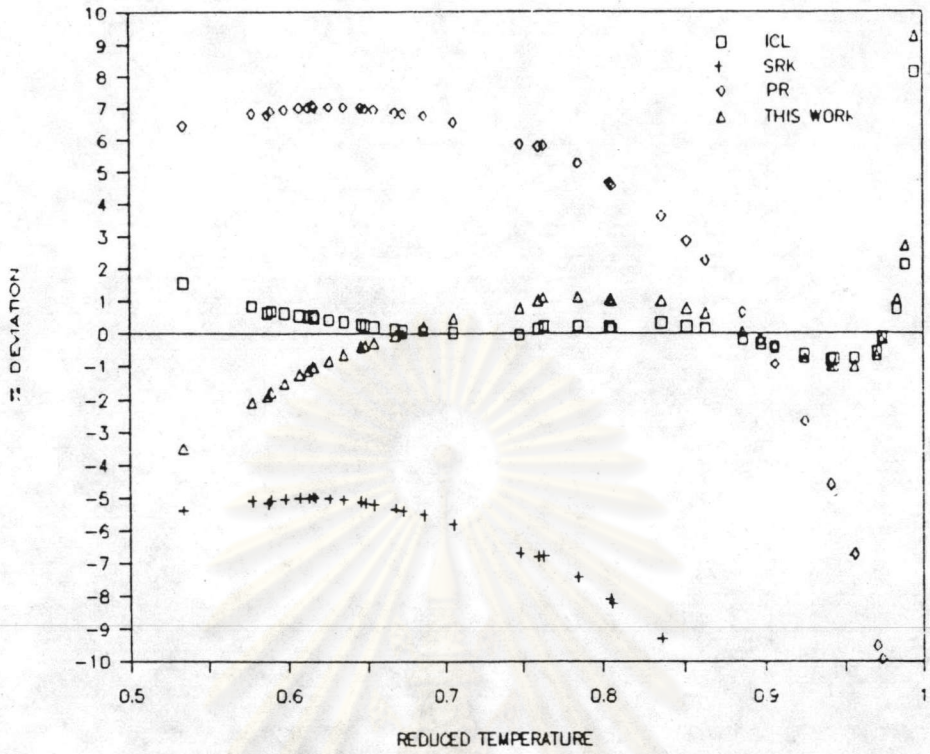

Figure 4.23 % Deviation in Saturated Liquid Volume for Propylene

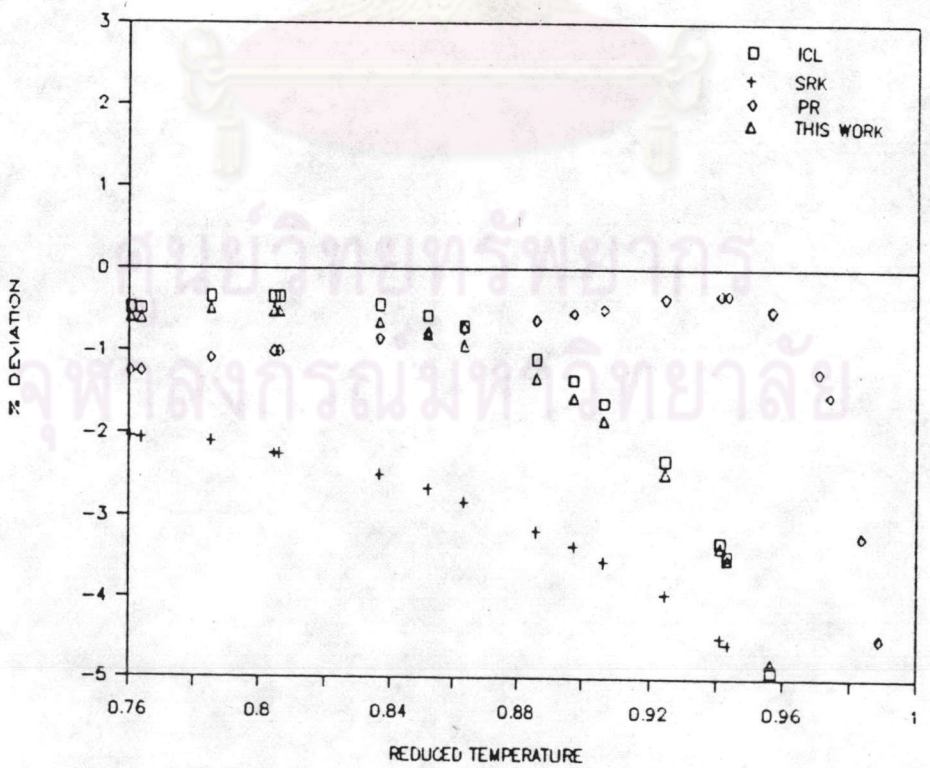

Figure 4.24 % Deviation in Saturated Vapor Volume for Propylene

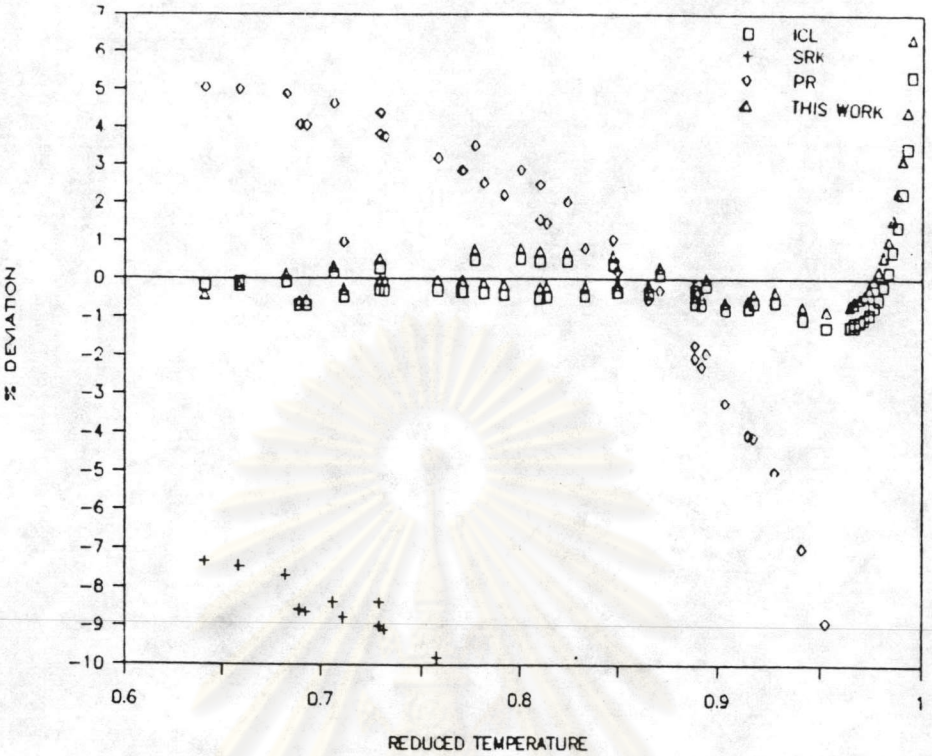

Figure 4.25 % Deviation in Saturated Liquid Volume for n-Butane

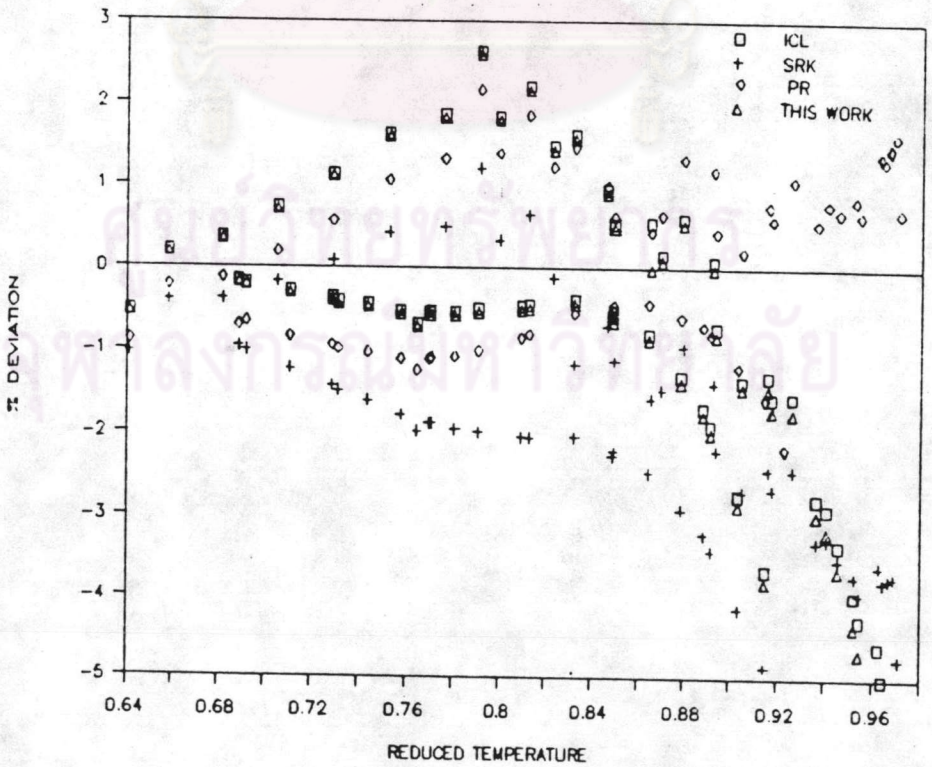

Figure 4.26 % Deviation in Saturated Vapor Volume for n-Butane

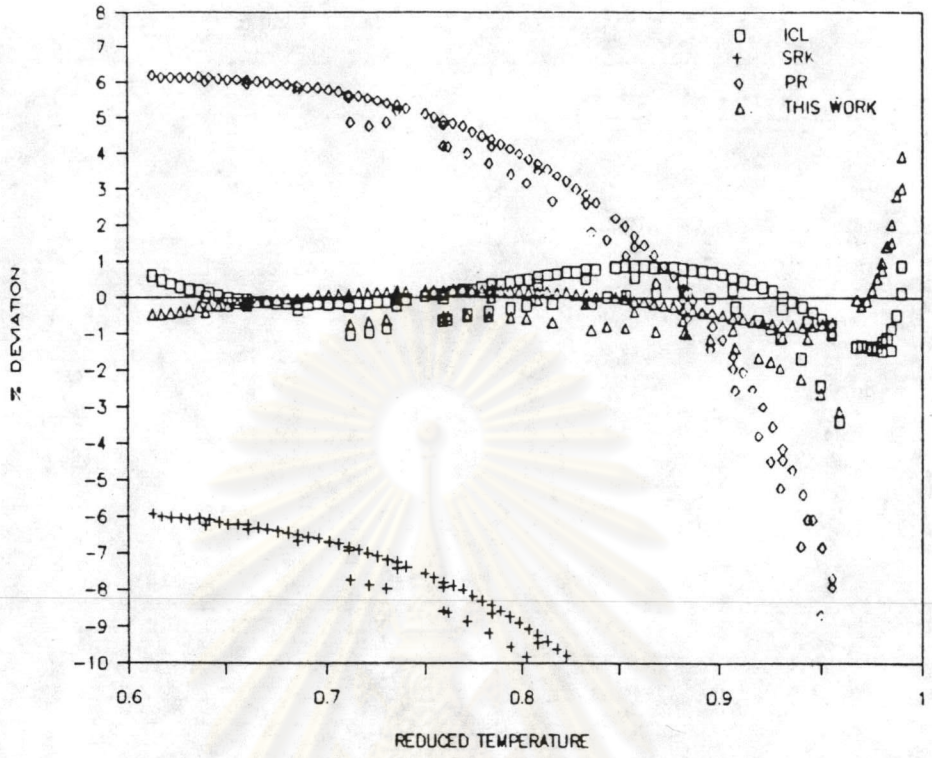

Figure 4.27 Deviation in Saturated Liquid Volume for iso-Butane

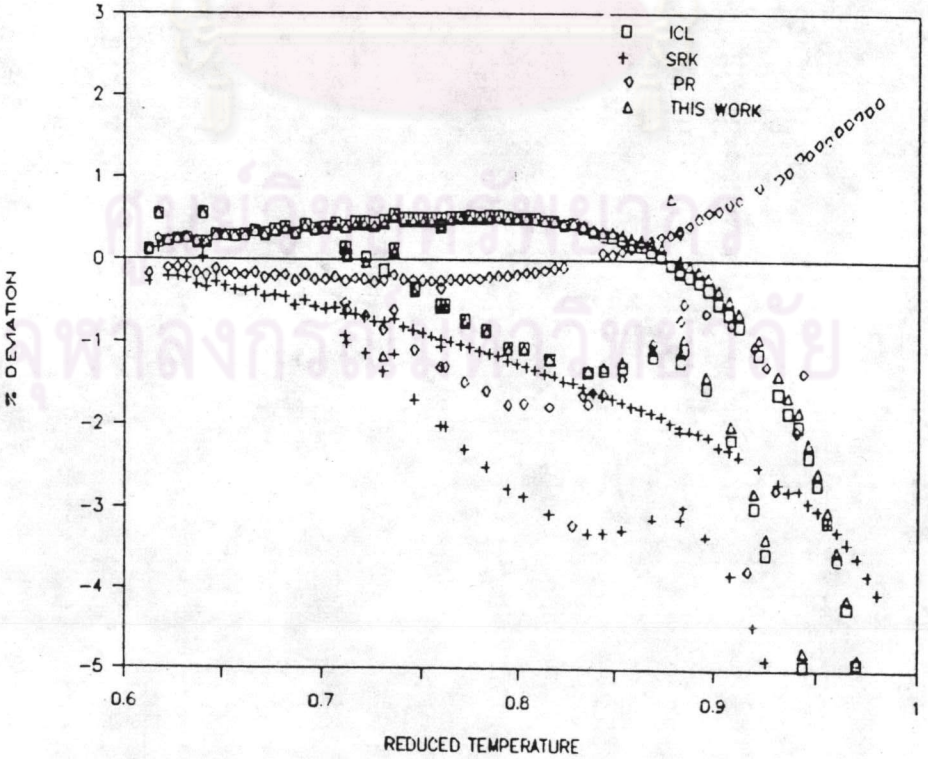

Figure 4.28 % Deviation in Saturated Vapor Volume for iso-Butane

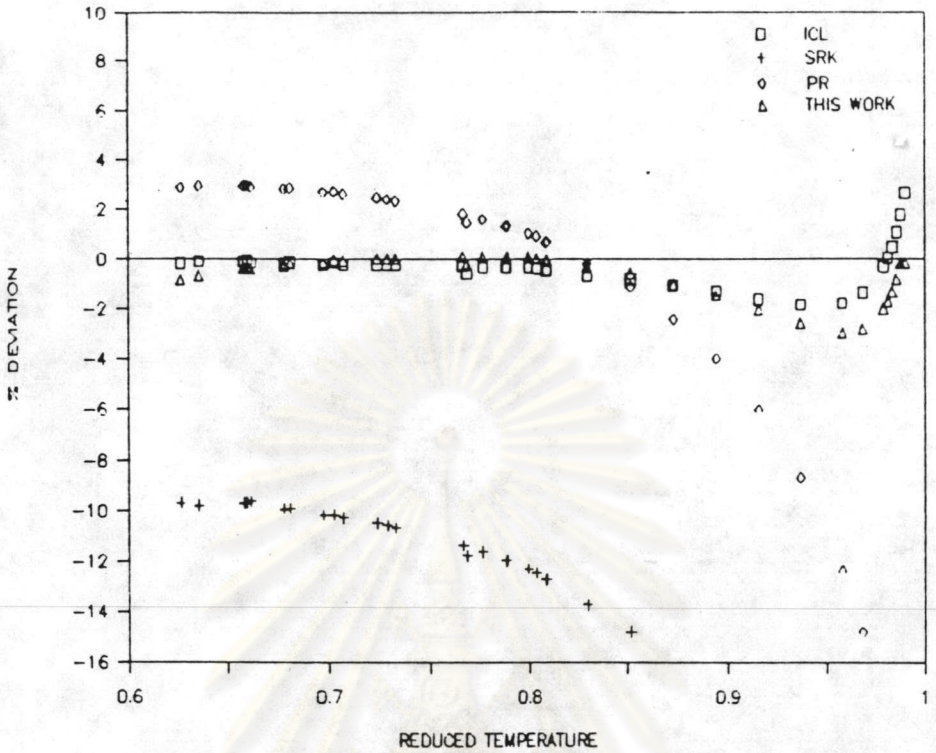

Figure 4.29 % Deviation in Saturated Liquid Volume for n-Pentane

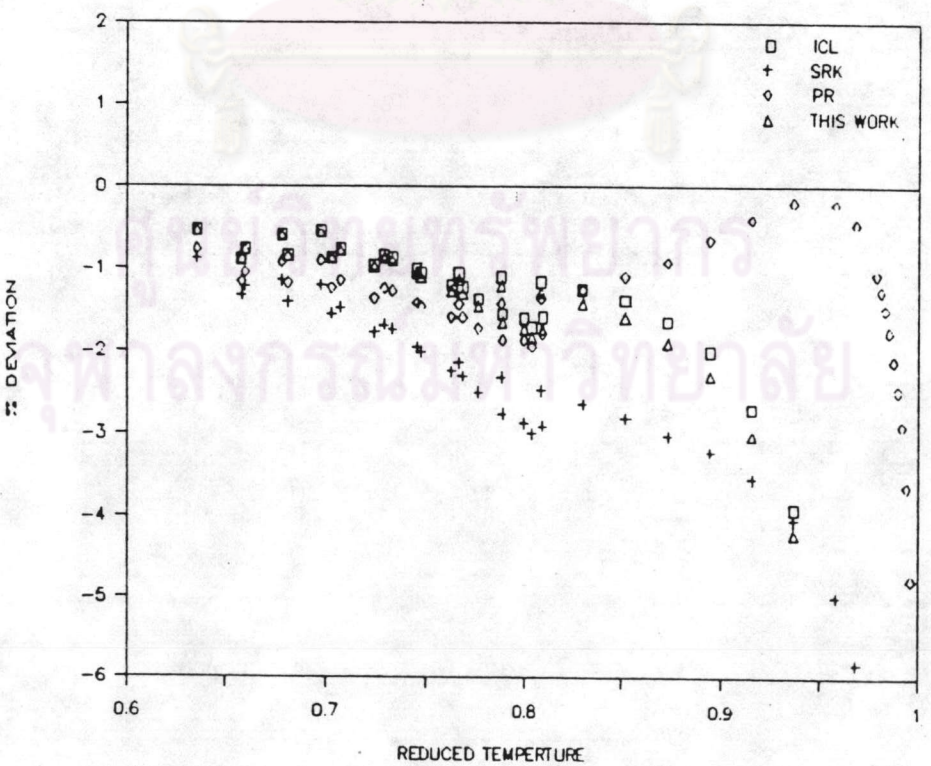

Figure 4.30 % Deviation in Saturated Vapor Volume for n-Pentane

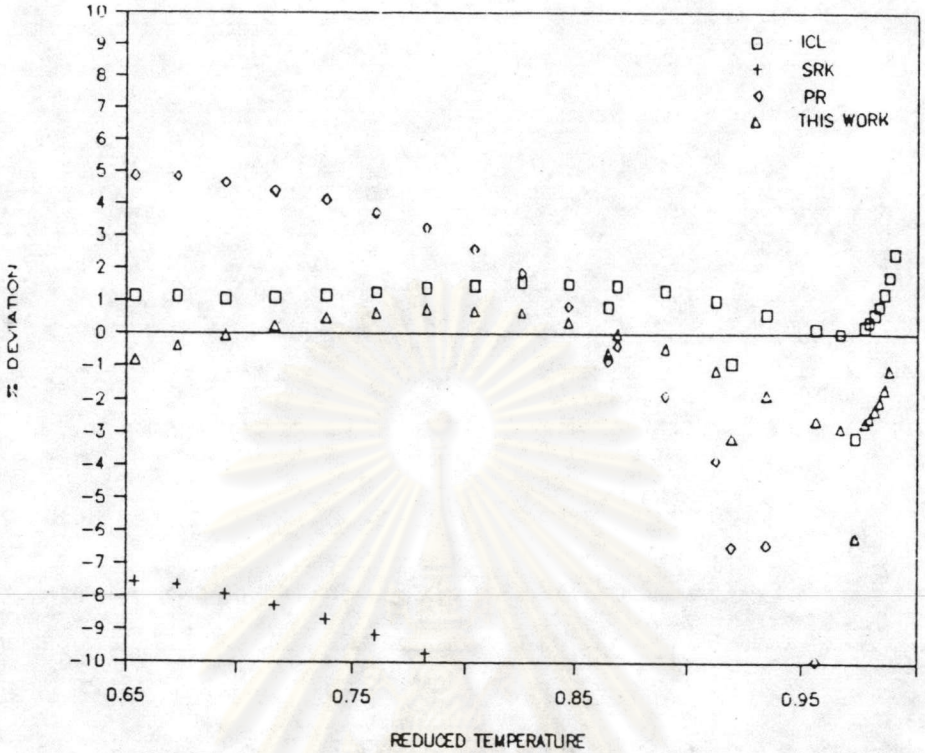

Figure 4.31 % Deviation in Saturated Liquid Volume for iso-Pentane

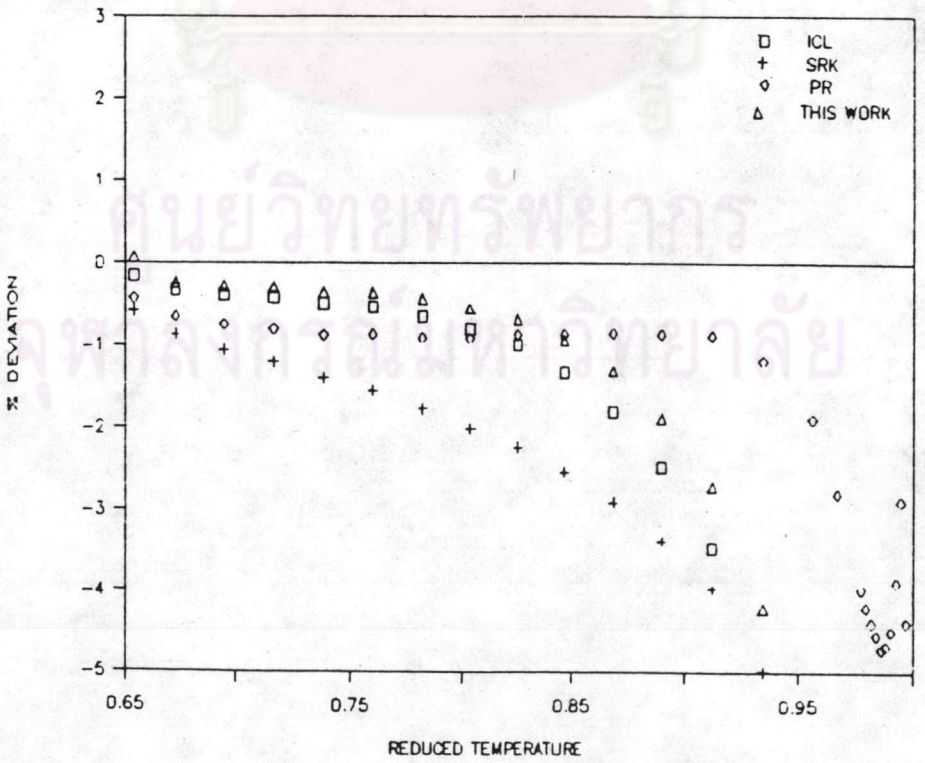

Figure 4.32 % Deviation in Saturated Vapor Volume for iso-Pentane

4.3 Vapor Pressure

The vapor pressures for ten pure component light hydrocarbons were calculated by the SRK, PR, and Equation (3.5) as shown in Figure 4.33 to 4.42. Numerical values of the vapor pressures are listed in Appendix B. These values were calculated by program called " **VAPPRESS** ", of Appendix A.

Figures 4.43 to 4.52 show percent deviations in vapor pressure for ten pure components investigated as a function of reduced temperature, which were calculated by SRK, PR, ICL and Equation (3.5).

% deviation (d_i) is defined as :

$$\% \text{ deviation} = \frac{(P_{exp} - P_{cal})}{P_{exp}} \cdot 100$$

where P_{exp} = experimental vapor pressure

P_{cal} = calculated vapor pressure

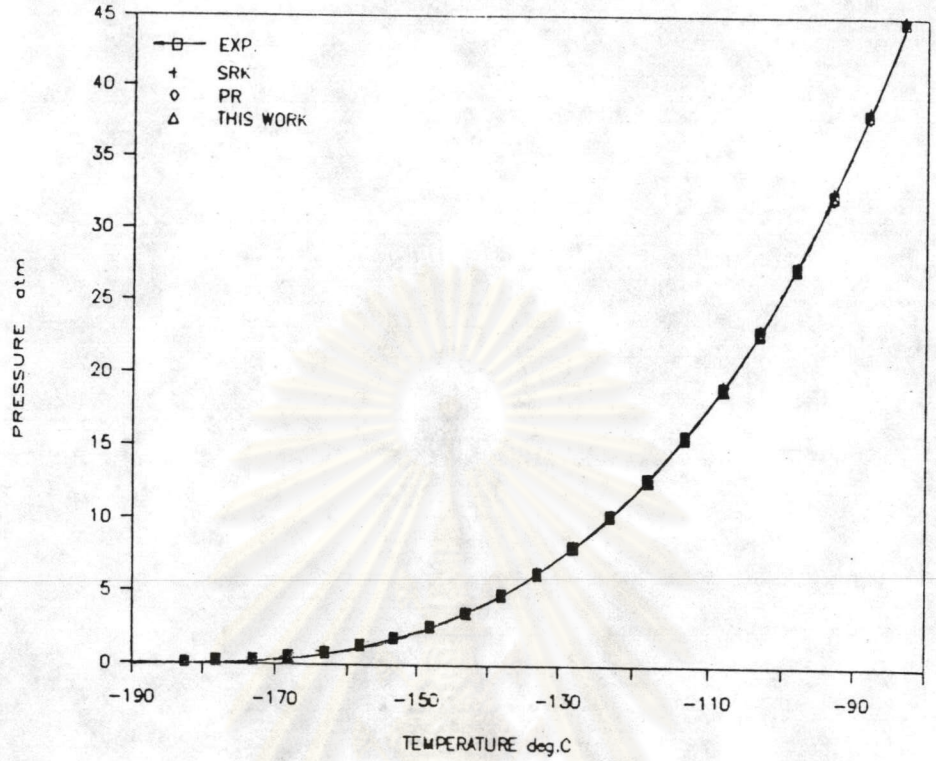

Figure 4.33 Vapor Pressure Curve of Methane

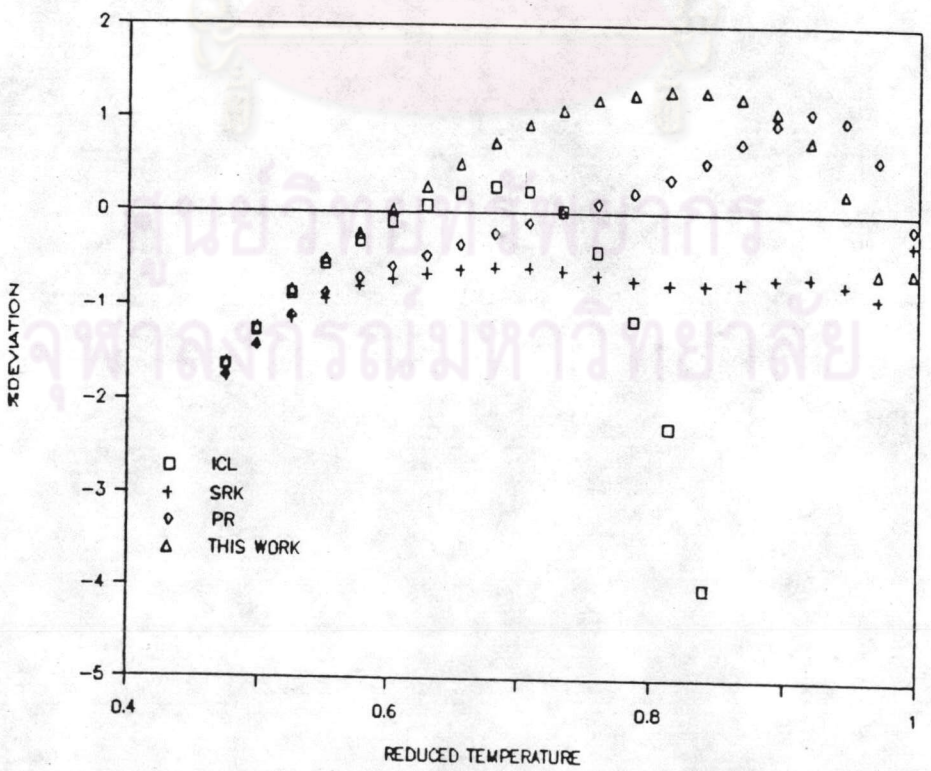

Figure 4.43 % Deviation in Vapor Pressure for Methane

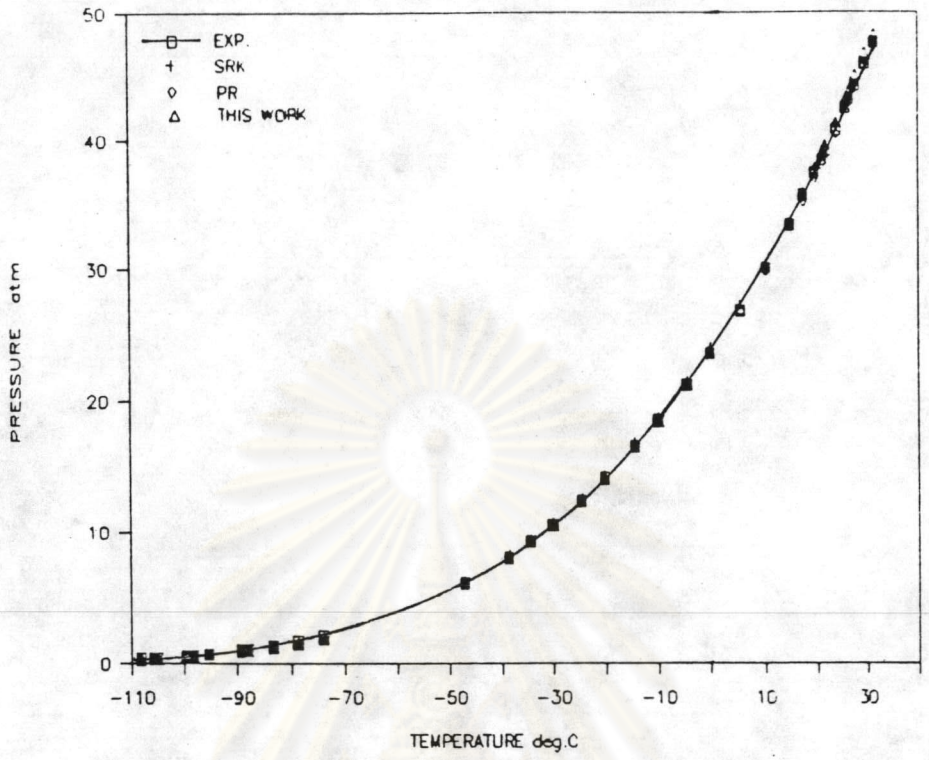

Figure 4.34 Vapor Pressure Curve of Ethane

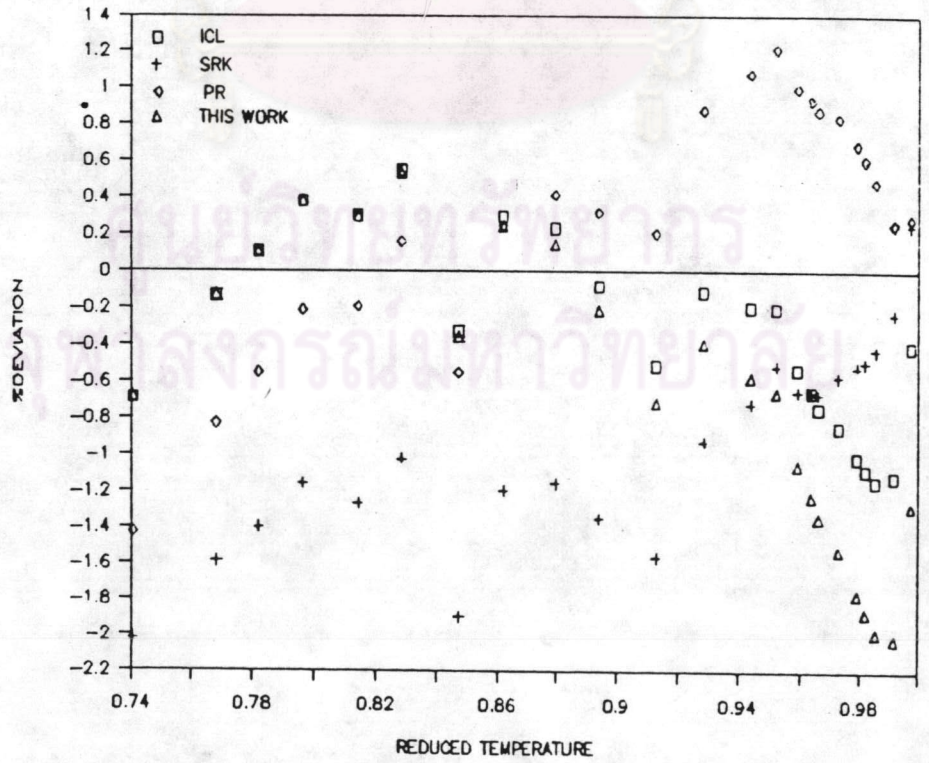

Figure 4.44 % Deviation in Vapor Pressure for Ethane

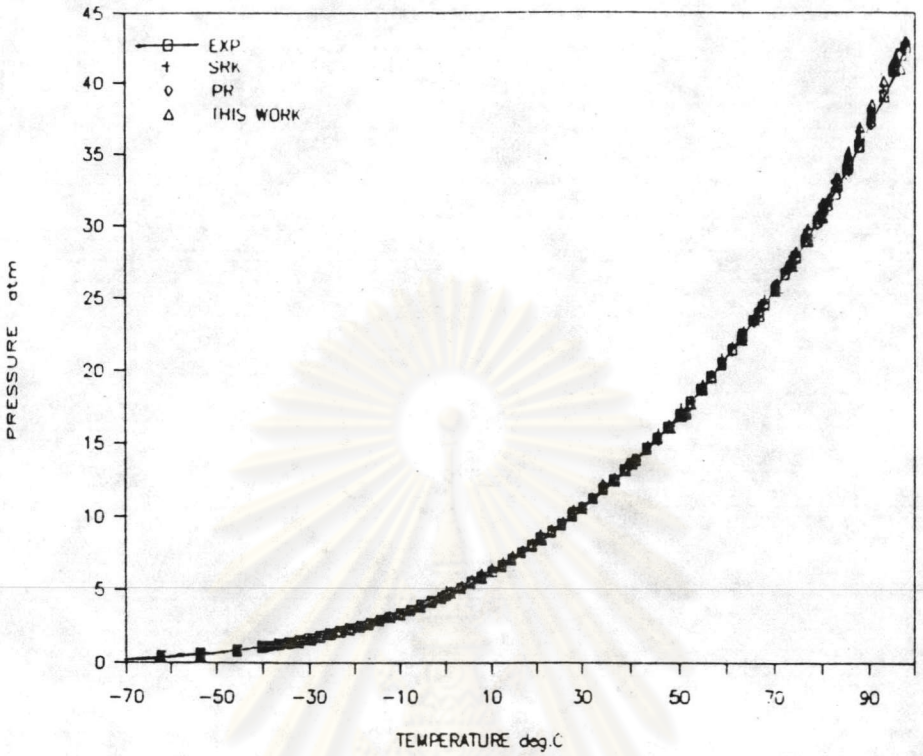

Figure 4.35 Vapor Pressure Curve of Propane

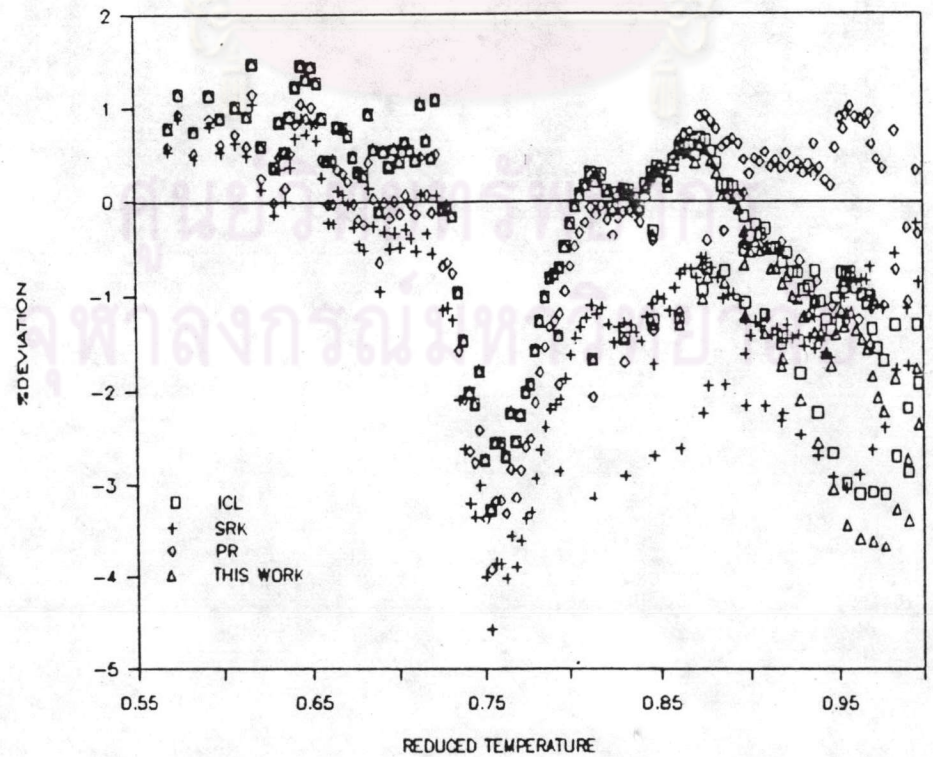

Figure 4.45 % Deviation in Vapor Pressure for Propane

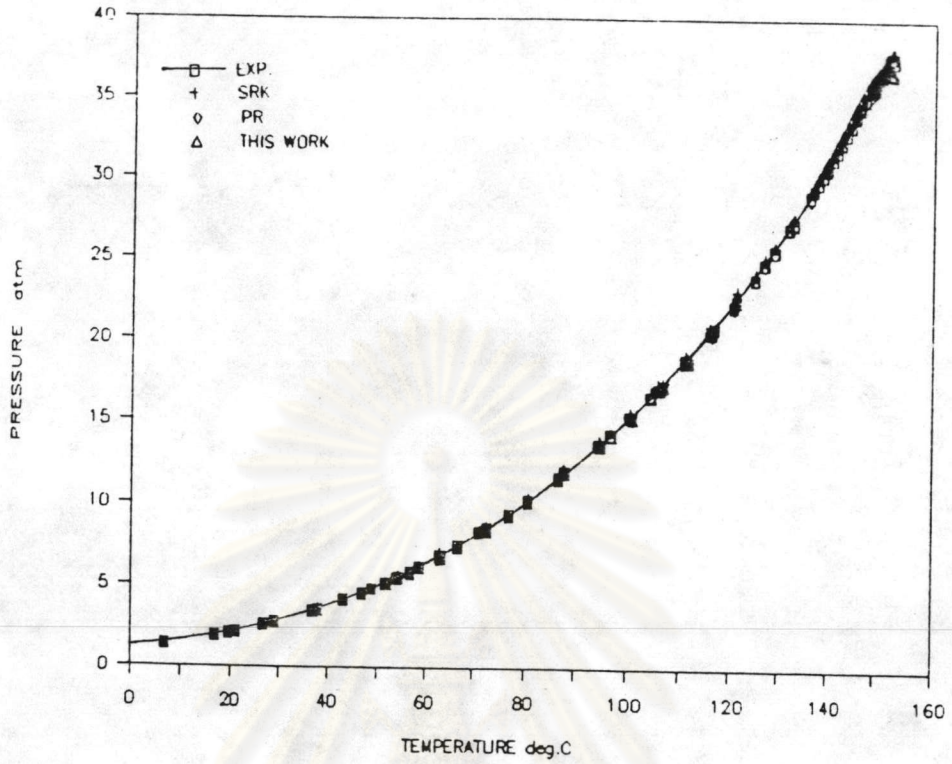

Figure 4.36 Vapor Pressure Curve of n-Butane

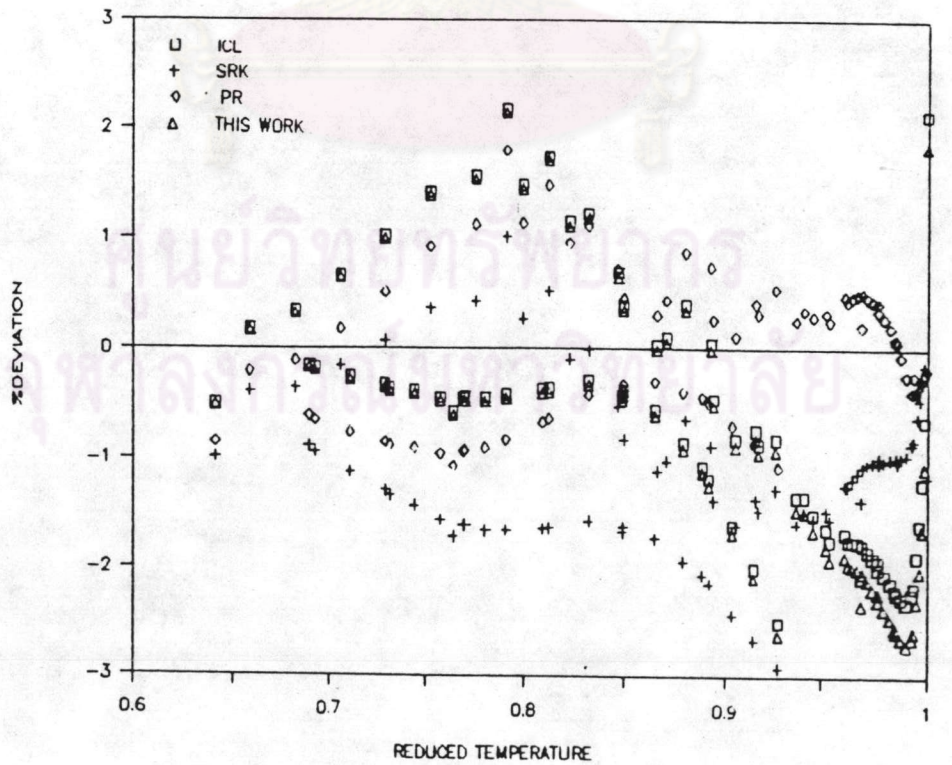

Figure 4.46 % Deviation in Vapor Pressure for n-Butane

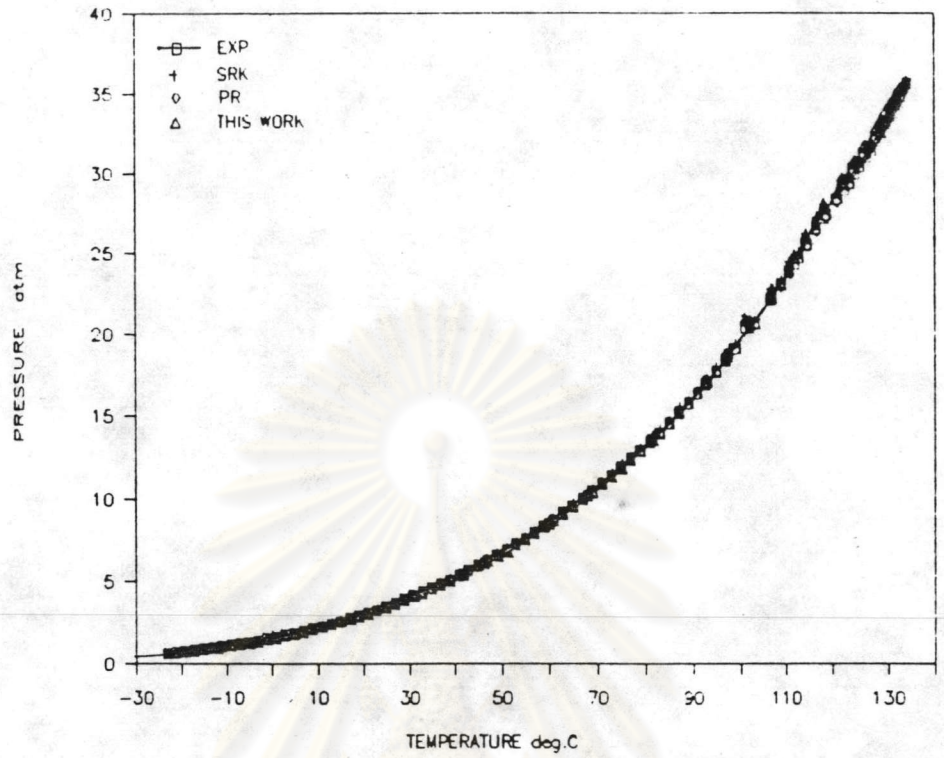

Figure 4.37 Vapor Pressure Curve of iso-Butane

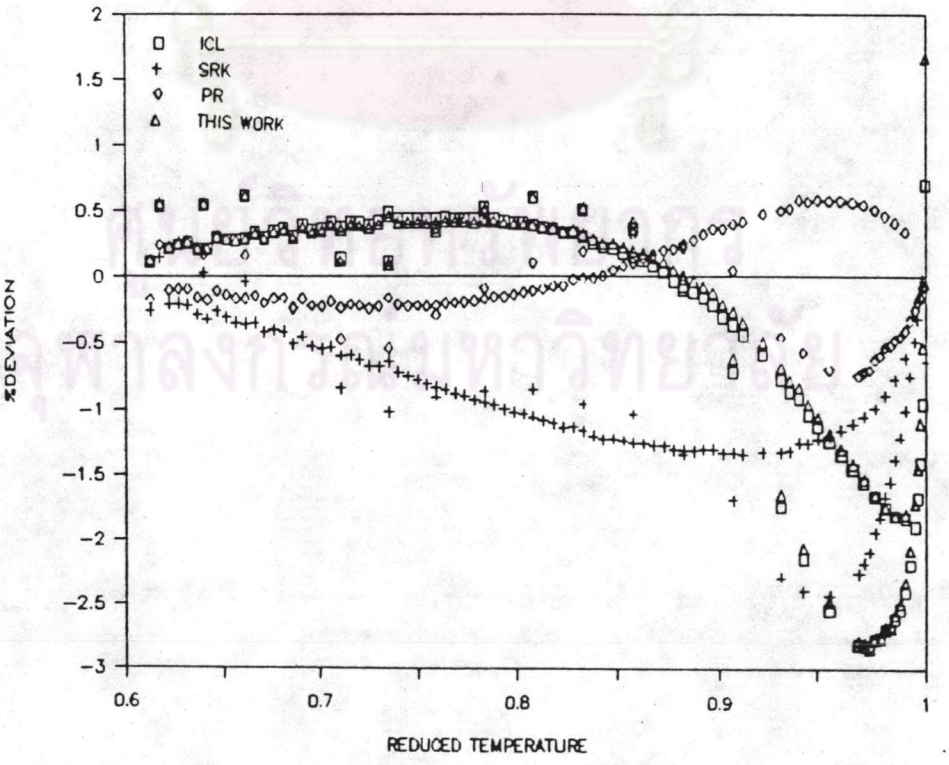

Figure 4.47 % Deviation in Vapor Pressure for iso-Butane

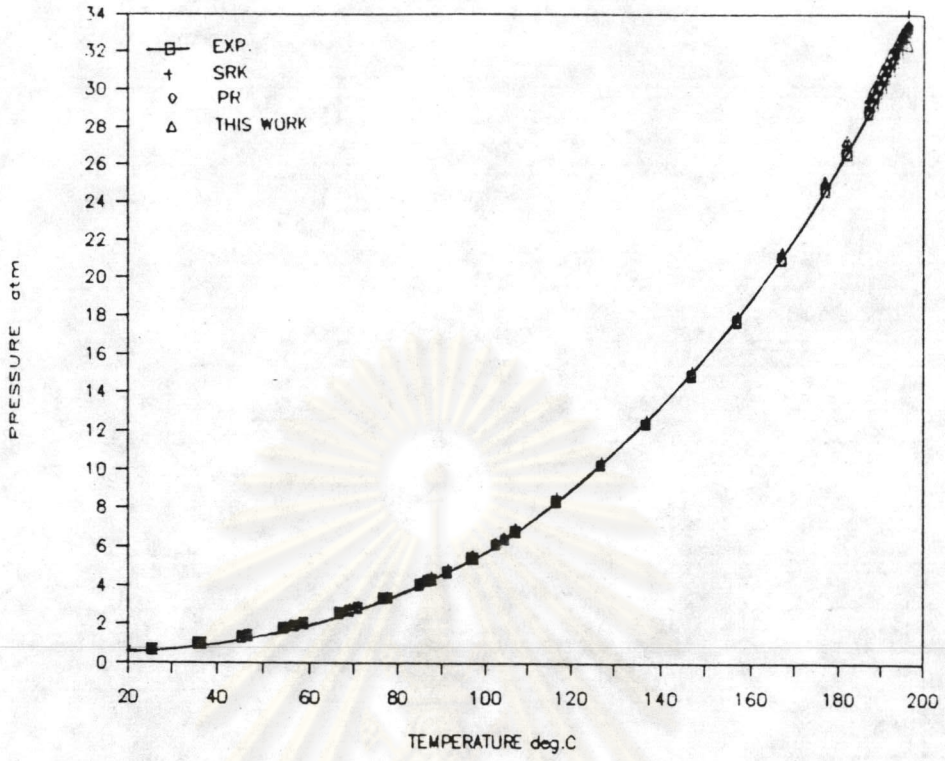

Figure 4.38 Vapor Pressure Curve of n-Pentane

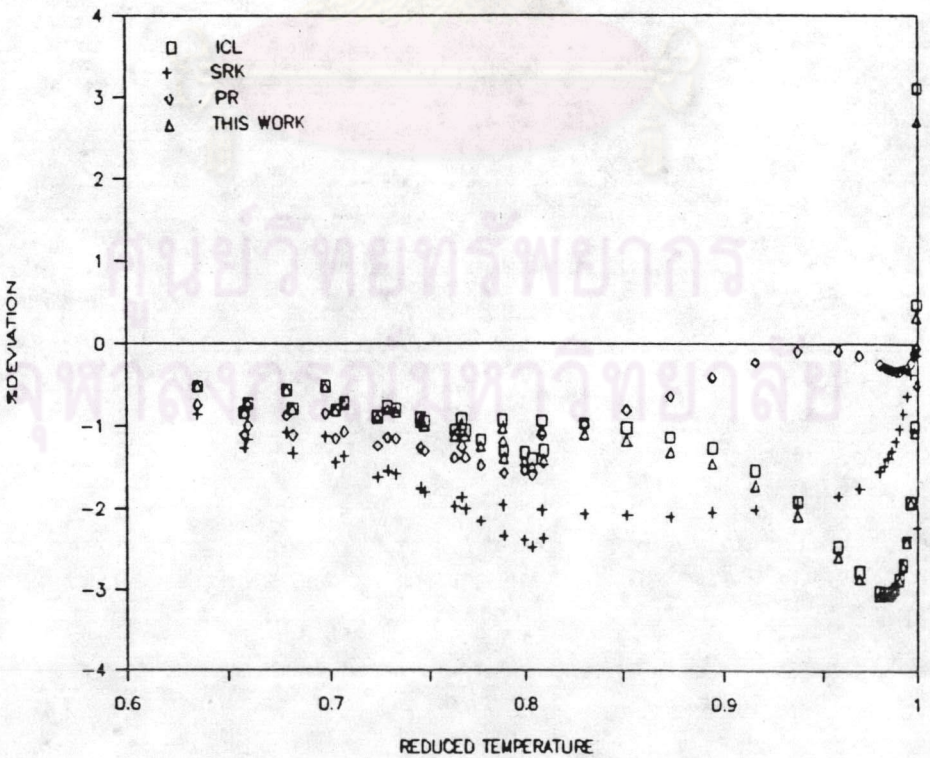

Figure 4.48 % Deviation in Vapor Pressure for n-Pentane

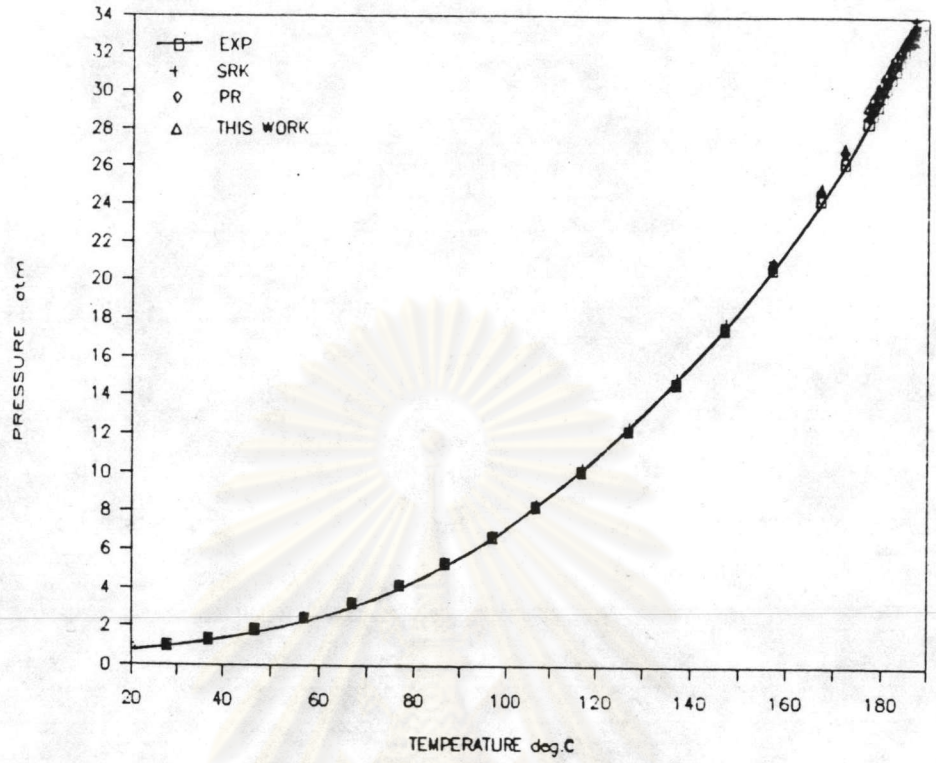

Figure 4.39 Vapor Pressure Curve of iso-Pentane

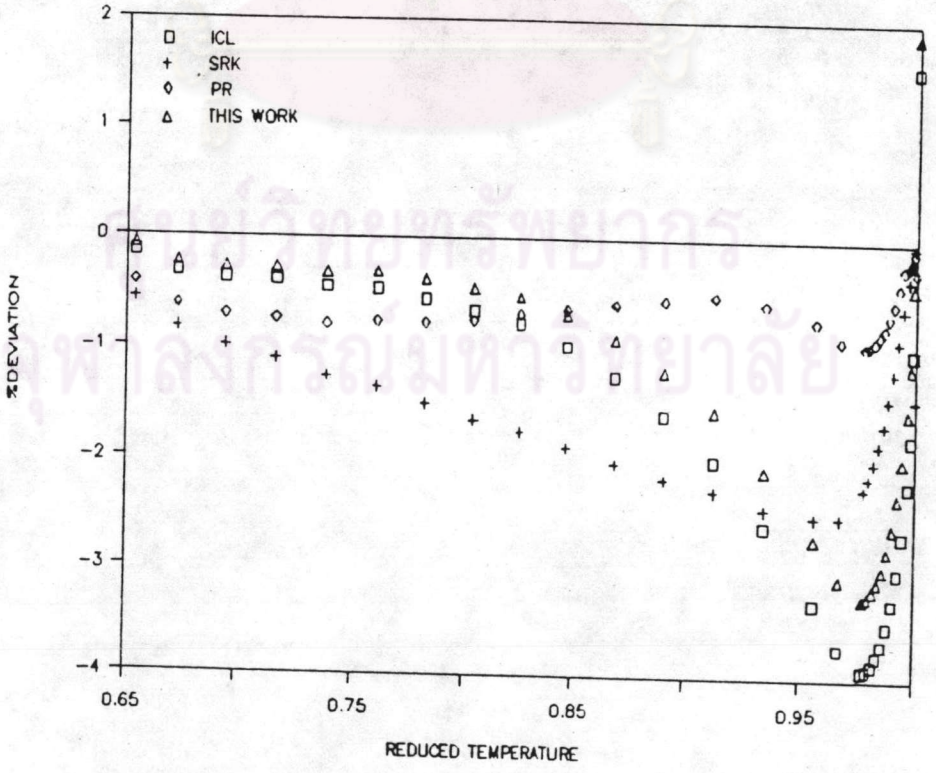

Figure 4.49 % Deviation in Vapor Pressure for iso-Pentane

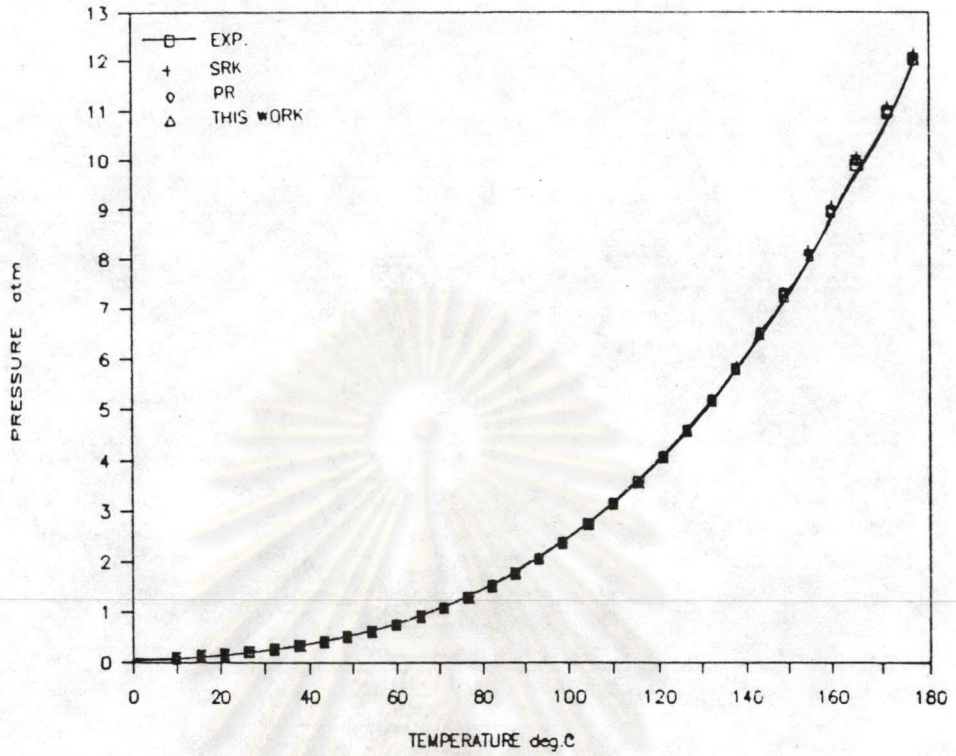

Figure 4.40 Vapor Pressure Curve of n-Hexane

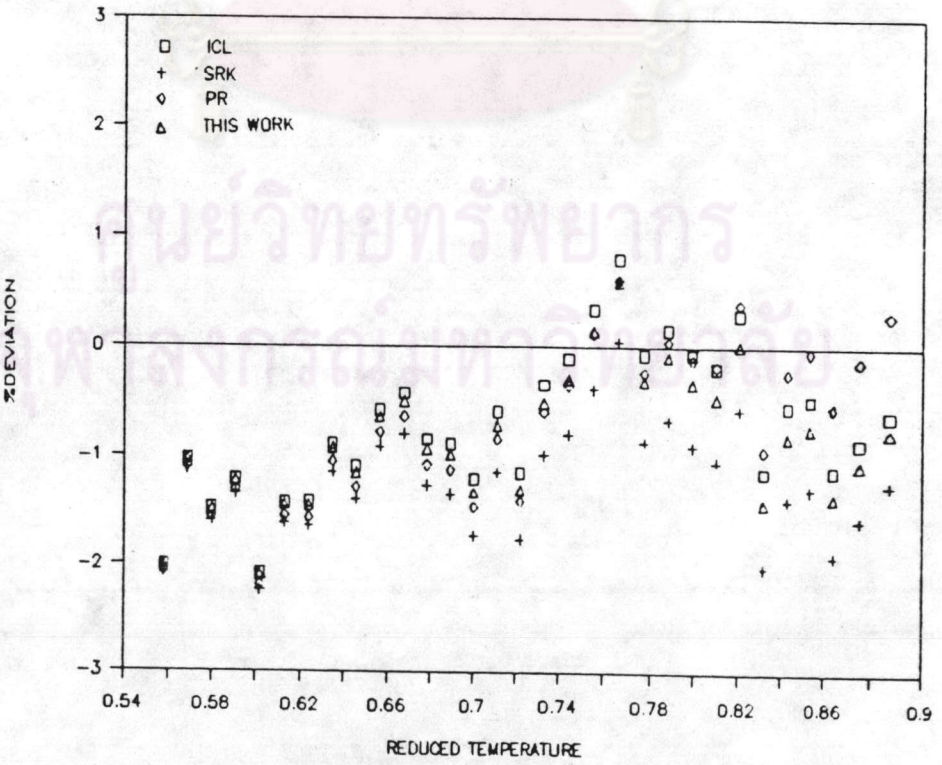

Figure 4.50 % Deviation in Vapor Pressure for n-Hexane

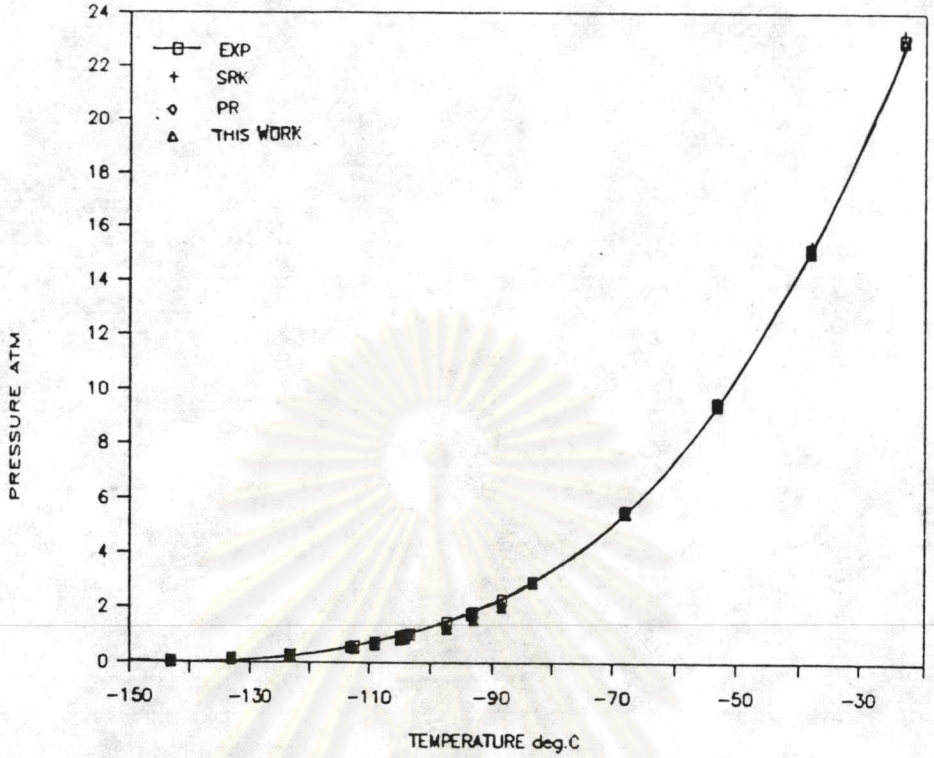

Figure 4.41 Vapor Pressure Curve of Ethylene

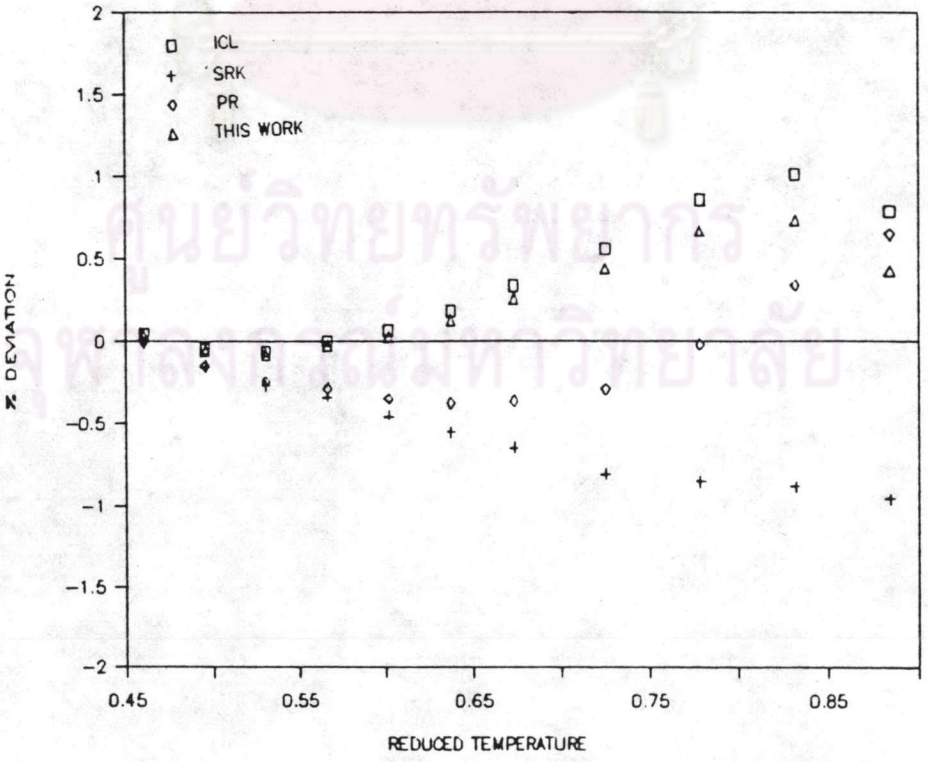

Figure 4.51 % Deviation in Vapor Pressure for Ethylene

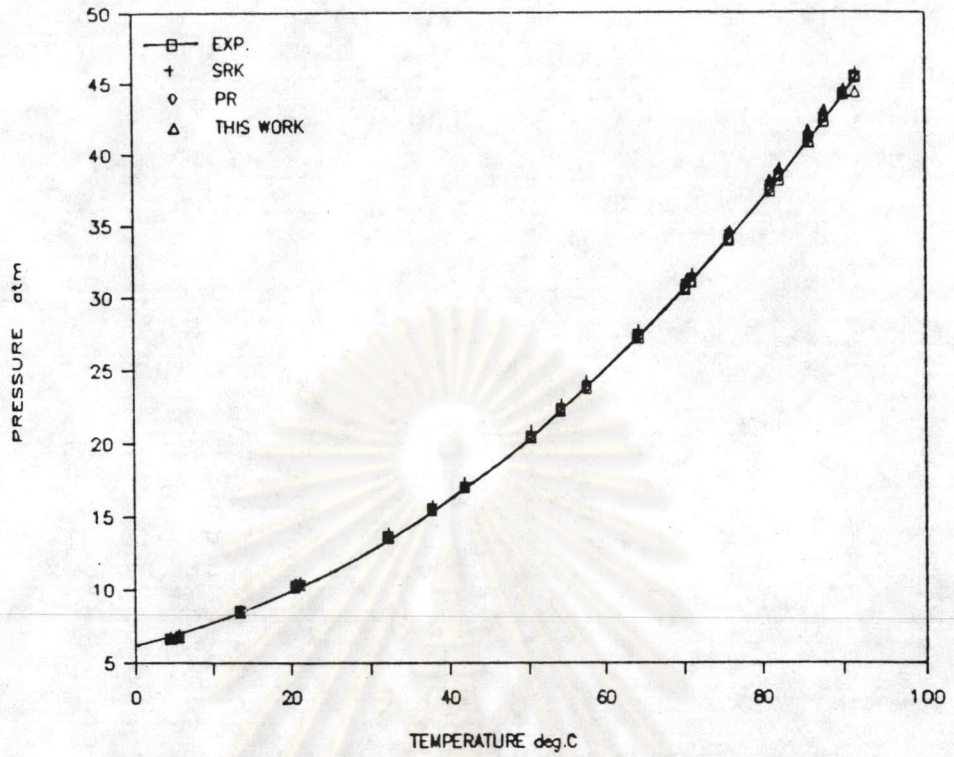

Figure 4.42 Vapor Pressure Curve of Propylene

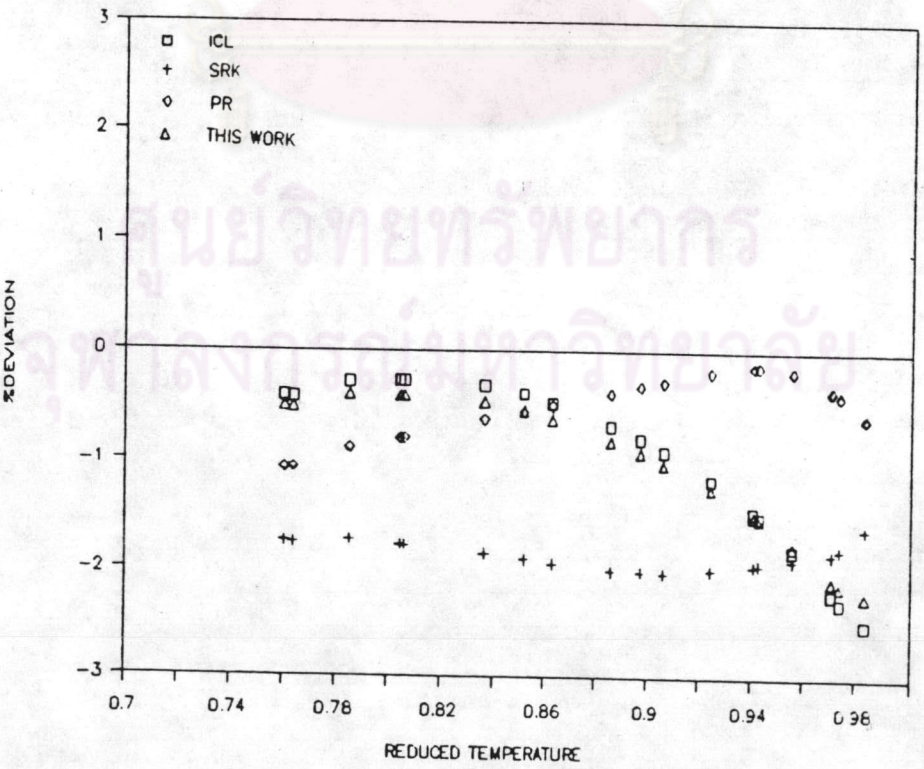

Figure 4.52 % Deviation in Vapor Pressure for Propylene

4.4 Compressibility Factor

Compressibility factors for a superheated vapor state for ethane, ethylene, propane, and propylene as shown in Figures 4.53 to 4.56 were calculated by Equation (3.5). These figures show correlations of compressibility (Z = PV/RT) and reduced pressures for reduced temperatures less than 1.2. Figures 4.53, 4.54, 4.55 and 4.56 provide comparisons of isotherms between experimental data and calculated values for Ethane at 100°C, 130°C, 160°C, for Ethylene at 15°C, 25°C, 50°C, for Propane at 100°C, 125°C, 150°C and for Propylene at 91.4°C, 100°C, 125°C respectively. Numerical values of the compressibility factors calculated by the SRK, PR, ICL, and Equation (3.5) are listed in Appendix B. These values were calculated by program called " DENSITY " of Appendix A.

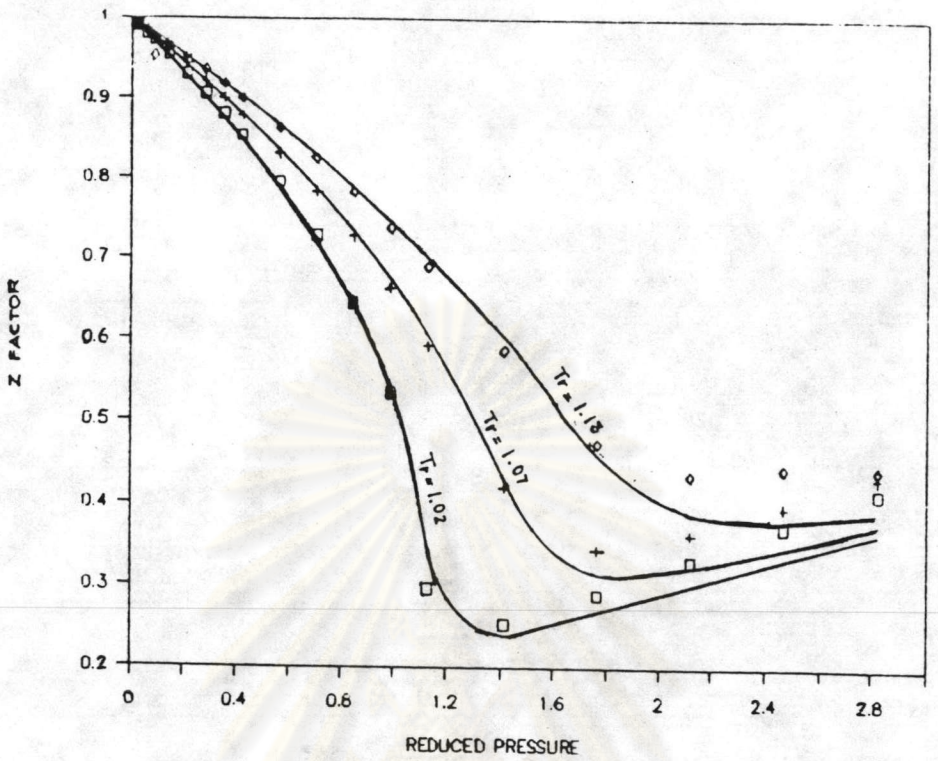

Figure 4.53 Compressibility factor for Ethane.
Points=experimental data, ——=calculated data

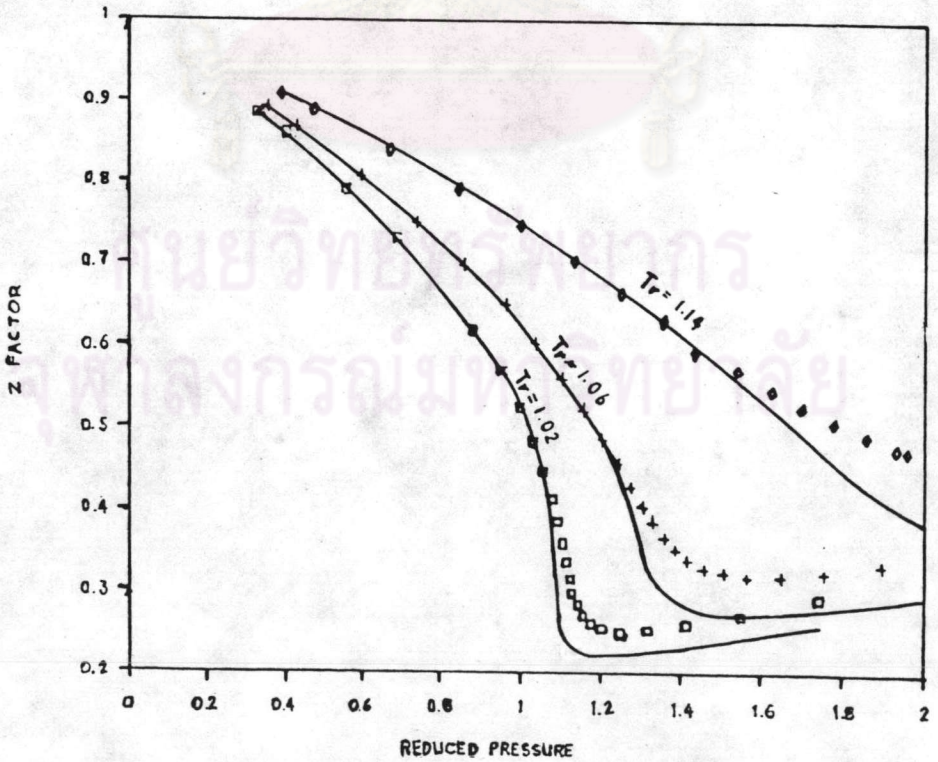

Figure 4.54 Compressibility factor for Ethylene
Points=experimental data, ——=calculated data

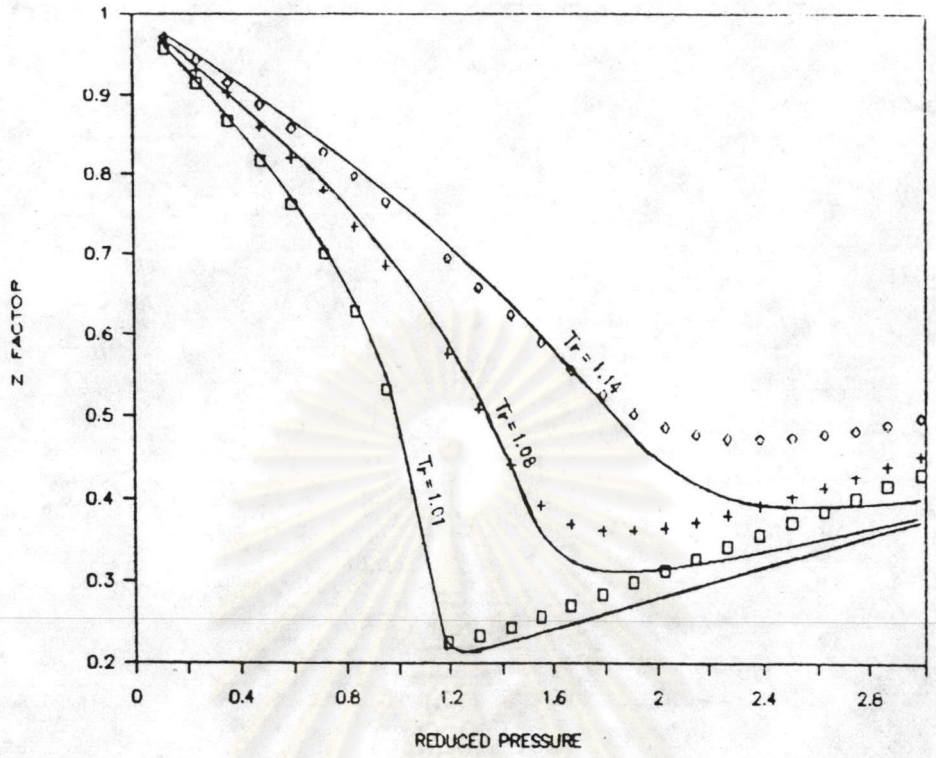

Figure 4.55 Compressibility factor for Propane

Points=experimental data, ——=calculated data

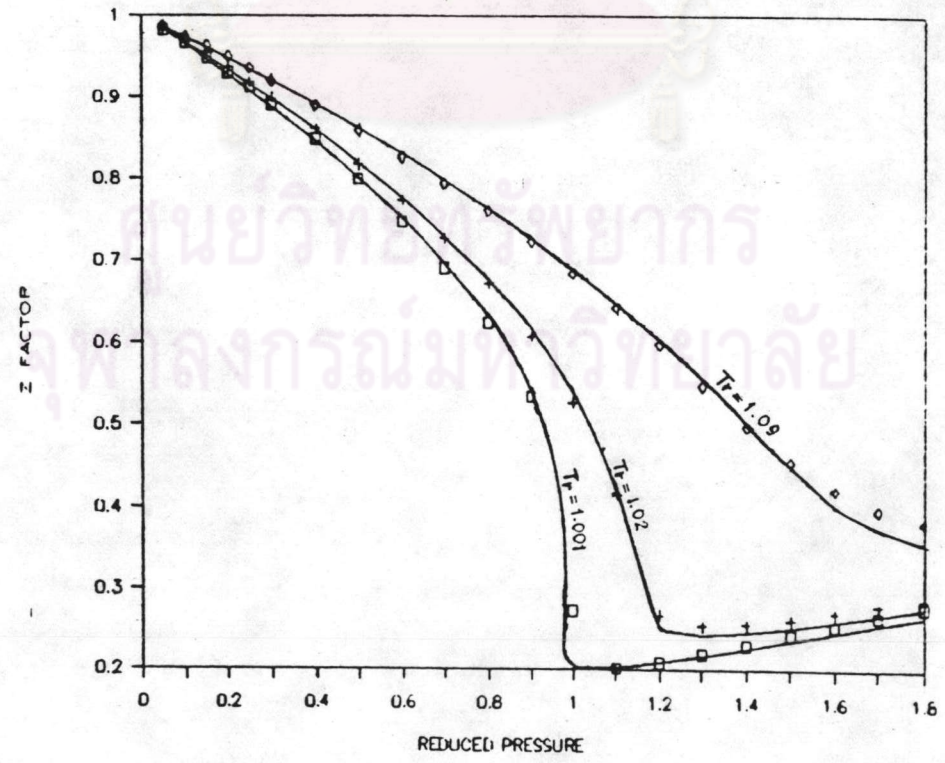

Figure 4.56 Compressibility factor for Propylene

Points=experimental data, ——=calculated data

4.5 Vapor-Liquid Equilibrium Calculations

Figures 4.57 to 4.60 show the comparison of predicted and experimental phase equilibrium for Ethane-Propane, Ethane-n-Butane, Ethane-iso-Butane, and Propylene-Propane binary systems. Figure 4.57 provides the comparison between the experimental data of Matschke (56) and the calculated values for the Ethane-Propane system at 310.94 °K, 333.16°K and 355.38°K. Figure 4.58 provides the comparison between the experimental data of Mehra et al.(57) and the calculated values for the Ethane-n-Butane system at 338.72°K, 366.49°K and 394.27°K. Figure 4.59 provides the comparison between the experimental data of Besserer (58) and the calculated values for the Ethane-iso-Butane system at 311.27°K, 344.49°K, and 377.44°K. Figure 4.60 provides the comparison between the experimental data of Harmens et al.(59) and the calculated values for the Propylene-Propane system at 250°K, 270°K, and 300°K.

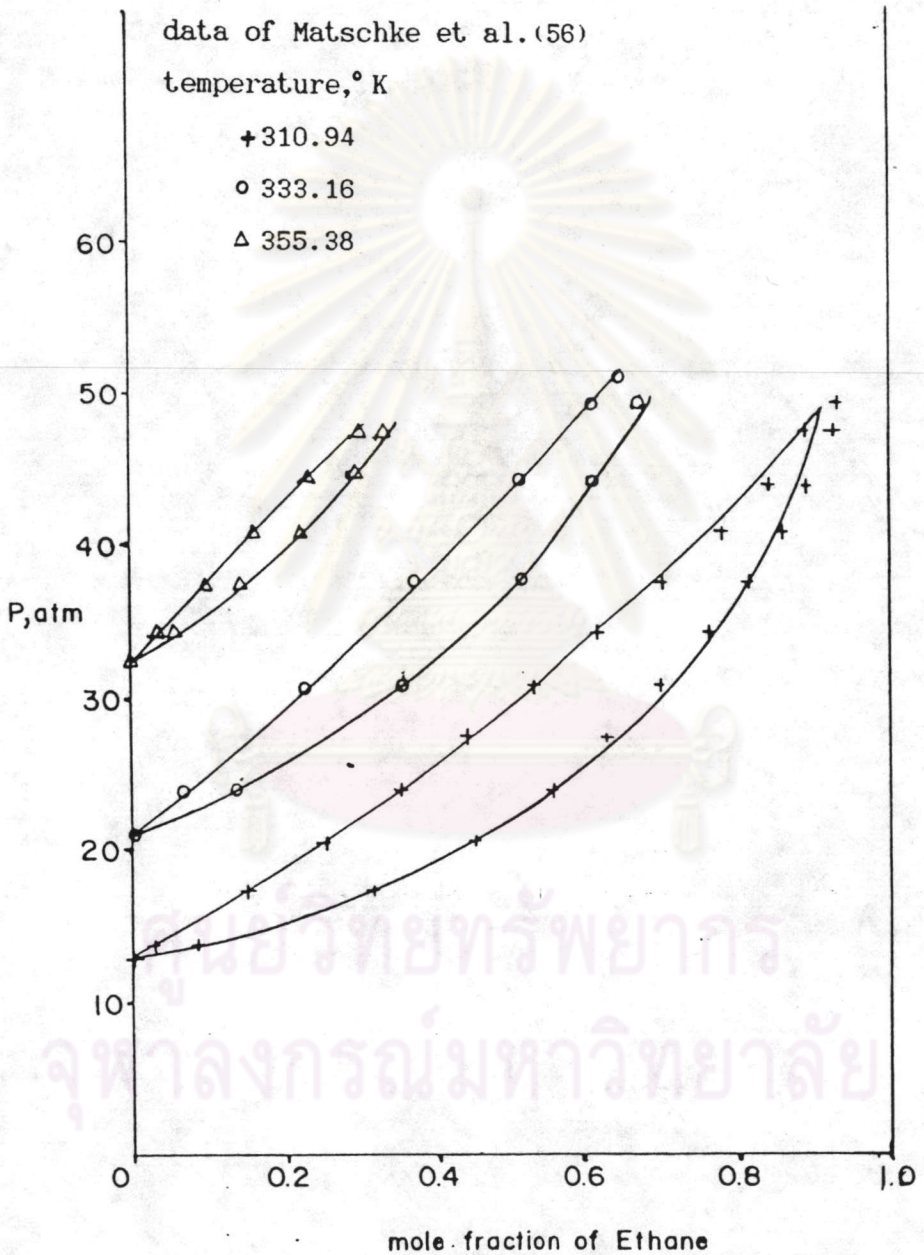

Figure 4.57 Calculated and experimental VLE values for Ethane-Propane system (——,calculated).

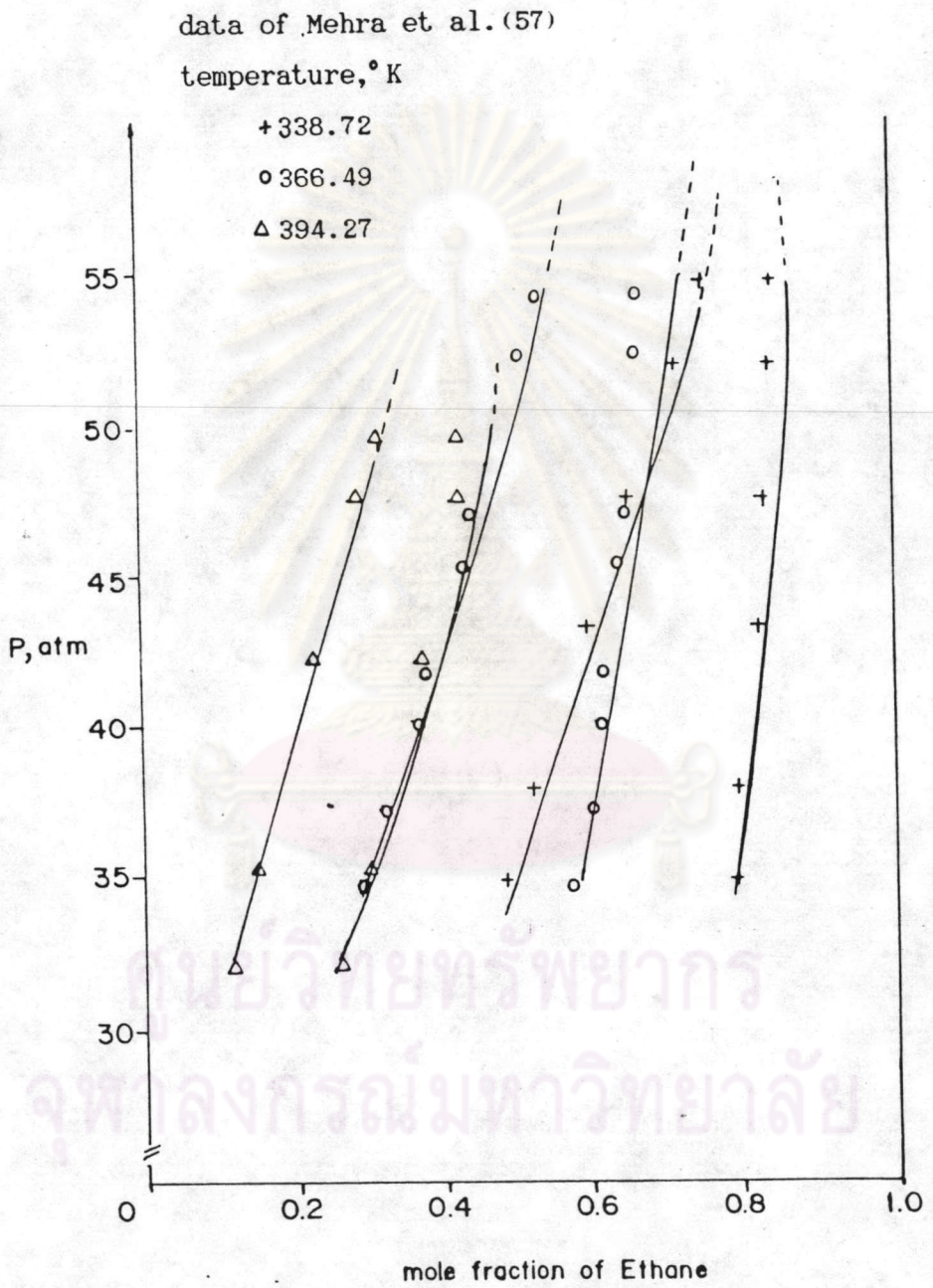

Figure 4.58 Calculated and experimental VLE values for Ethane-n-Butane system (——,calculated).

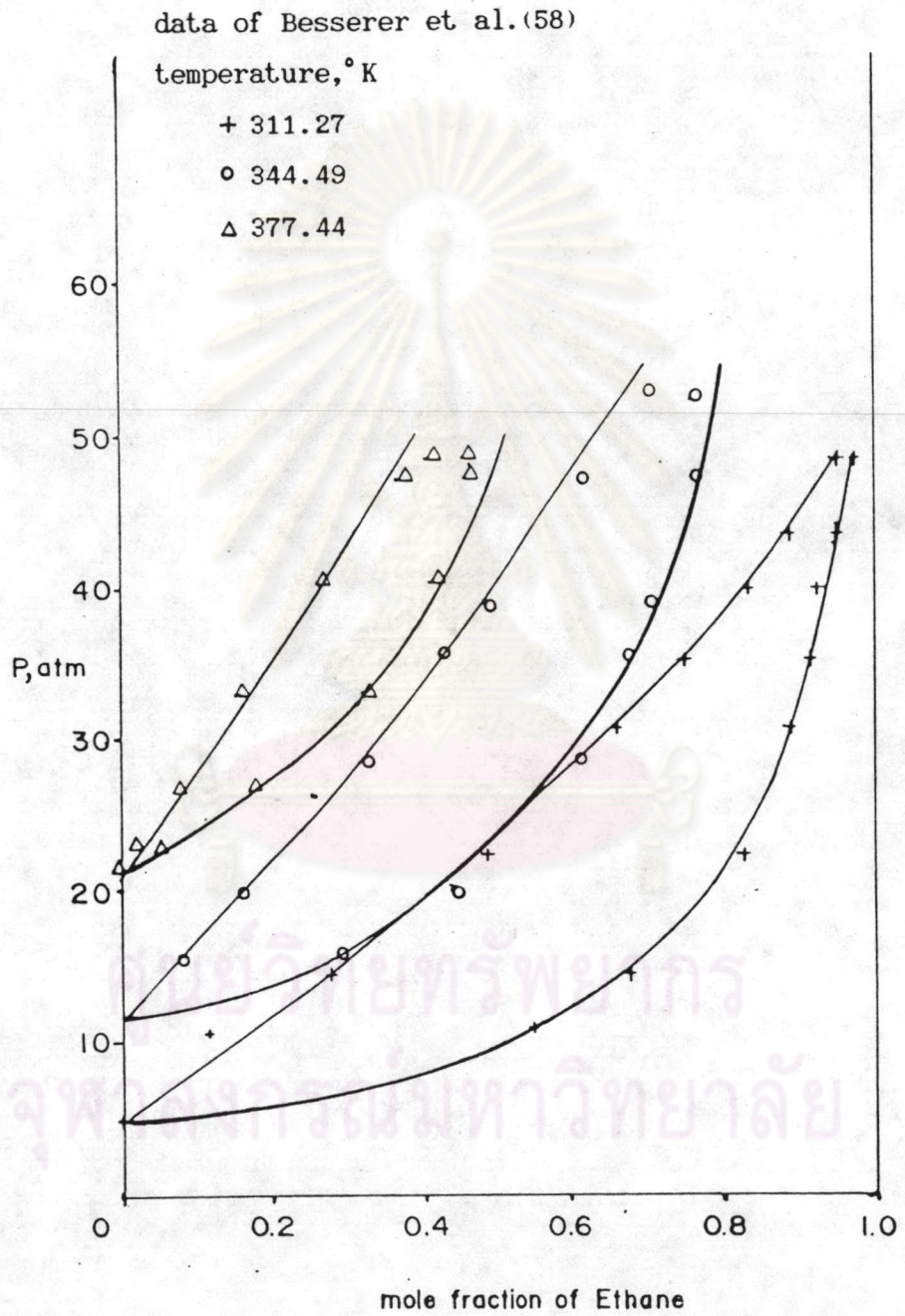

Figure 4.59 Calculated and experimental VLE values for Ethane-iso-Butane system (——,calculated).

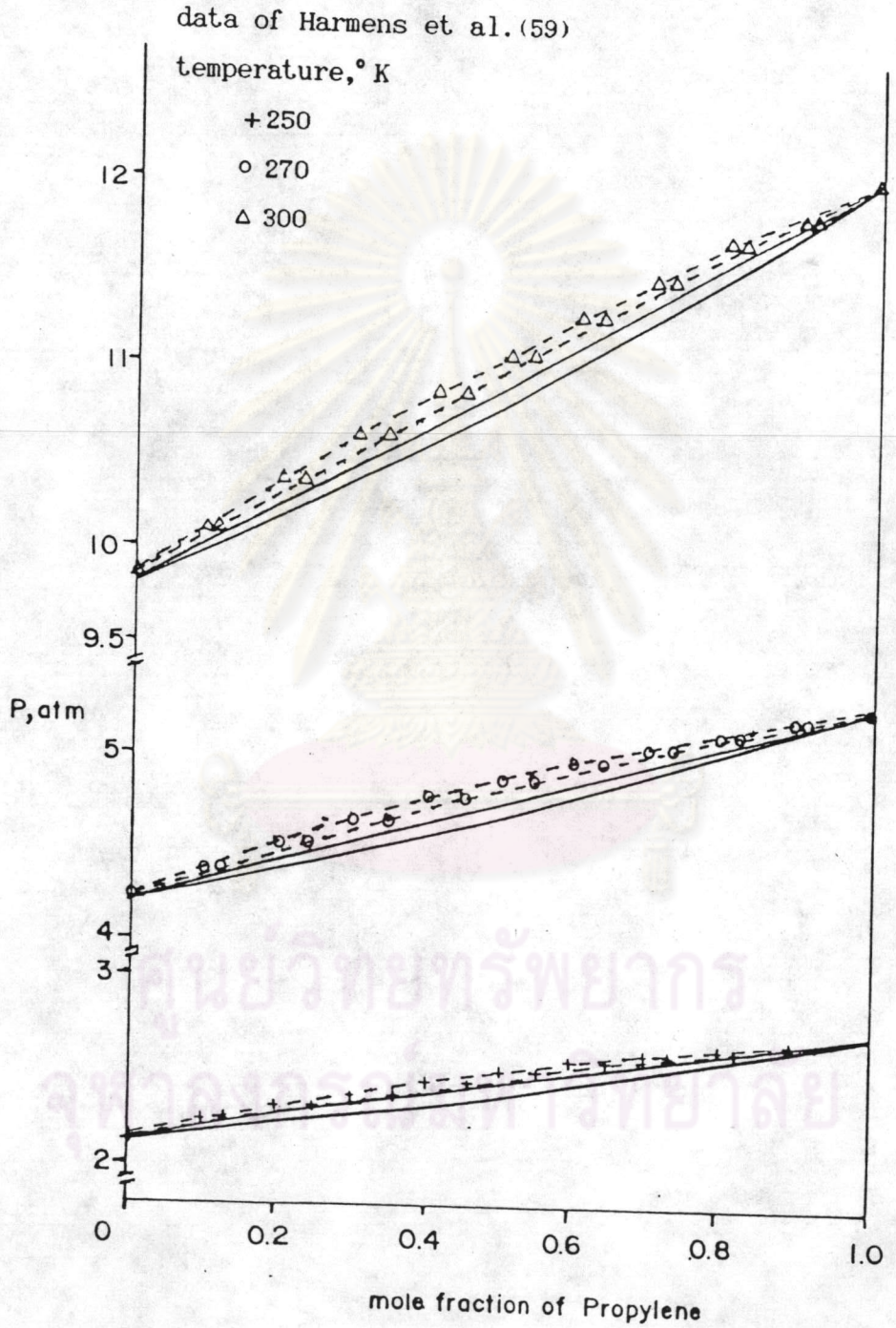

Figure 4.60 Calculated and experimental VLE values for Propylene-Propane system (——,calculated).

4.6 Another Modified Hard-Sphere Equation of State

4.6.1 The Temperature-Dependence Parameters

Based on the another modified hard sphere equation of state (Equation (3.34)) and the procedure in Figure 3.1 with the use of saturated liquid volume data, the temperature-dependent parameters Ω_a and Ω_b are evaluated for pure components, Methane, Ethane, Propane, n-Butane, iso-Butane, n-Pentane, iso-Pentane, n-Hexane, Ethylene and Propylene. The values of the parameters were correlated in terms of reduced temperature (T_r) for all the pure components and were further correlated by means of Equations (3.38) and (3.39). The coefficients a_i and b_i were determined using the method of least-squares and are reported in Table 4.3 for the ten pure components investigated.

4.6.2 Saturated Liquid and Saturated Vapor Volumes

Figures 4.61 to 4.65 show percent deviations in saturated liquid and vapor volume for pure component light hydrocarbons as a function of reduced temperature, which were calculated by the Equation (3.34). It can be seen that the Equation (3.34) predicted the saturated liquid volume which generally agree very well with the experimental data. But the Equation (3.34) gives a large deviations between the calculated and the experimental values of saturated vapor volumes. So that the Equation (3.34) is not suitable for thermodynamic properties calculations in this investigated. Numerical values of the saturated liquid and vapor volumes are reported in Appendix B.

Table 4.3 Values of the Coefficients ai and bi of Equations (3.38) & (3.39) Determined by the Least-Squares Method.

Compound	a0	a1	a2	b0	b1	b2	Ref
Methane	0.82791	0.35862	-0.67024	0.14413	0.15685	-0.20033	(27)-(29)
Ethane	0.85044	0.37813	-0.71587	0.11637	0.21363	-0.22996	(30)-(32)
Propane	0.87558	0.38262	-0.74885	0.10423	0.24063	-0.24575	(34)-(37)
n-Butane	1.01816	0.05804	-0.56137	0.12338	0.18667	-0.20956	(38)-(40)
i-Butane	0.93588	0.27109	-0.69140	0.10423	0.24030	-0.24391	(41)-(43)
n-Pentane	0.91396	0.35501	-0.75779	0.08279	0.27910	-0.26228	(44),(45)
i-Pentane	1.00877	0.13018	-0.62381	0.10778	0.22693	-0.23424	(46),(47)
n-Hexane	1.12353	-0.25654	-0.33564	0.10768	0.18948	-0.19480	(48),(49)
Ethylene	0.74234	0.68254	-0.93806	0.09794	0.26785	-0.27017	(32),(51)
Propylene	1.12787	-0.28830	-0.31157	0.13391	0.15914	-0.19024	(32),(52),(53)

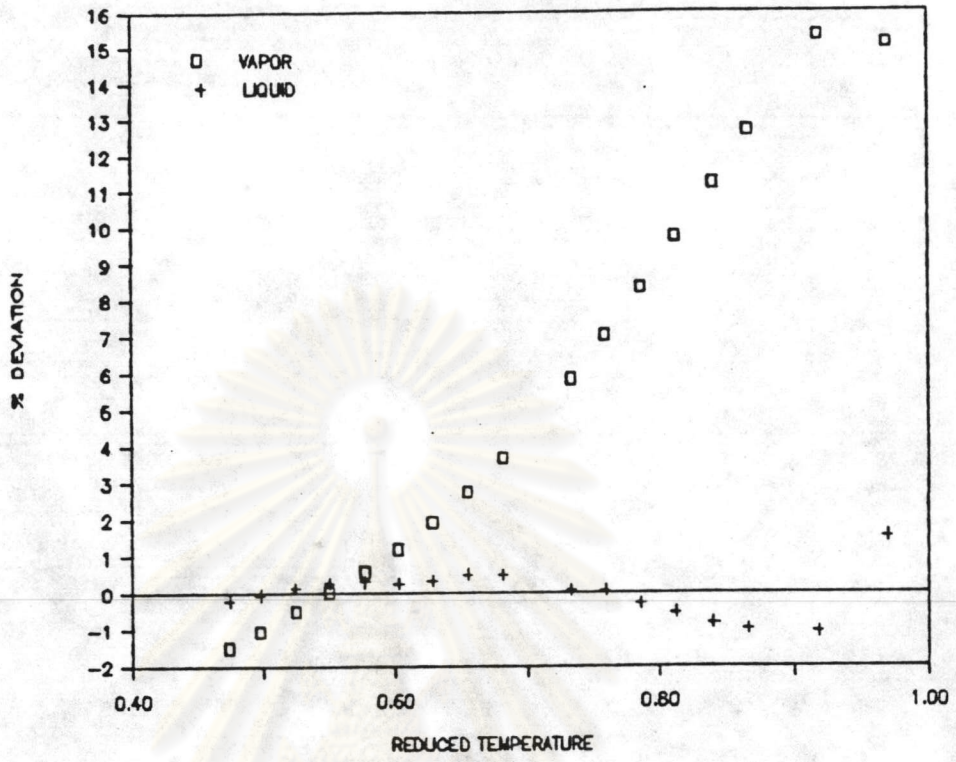

Figure 4.61 % Deviation in Saturated Volume for Methane (calculated by Equation (3.34)).

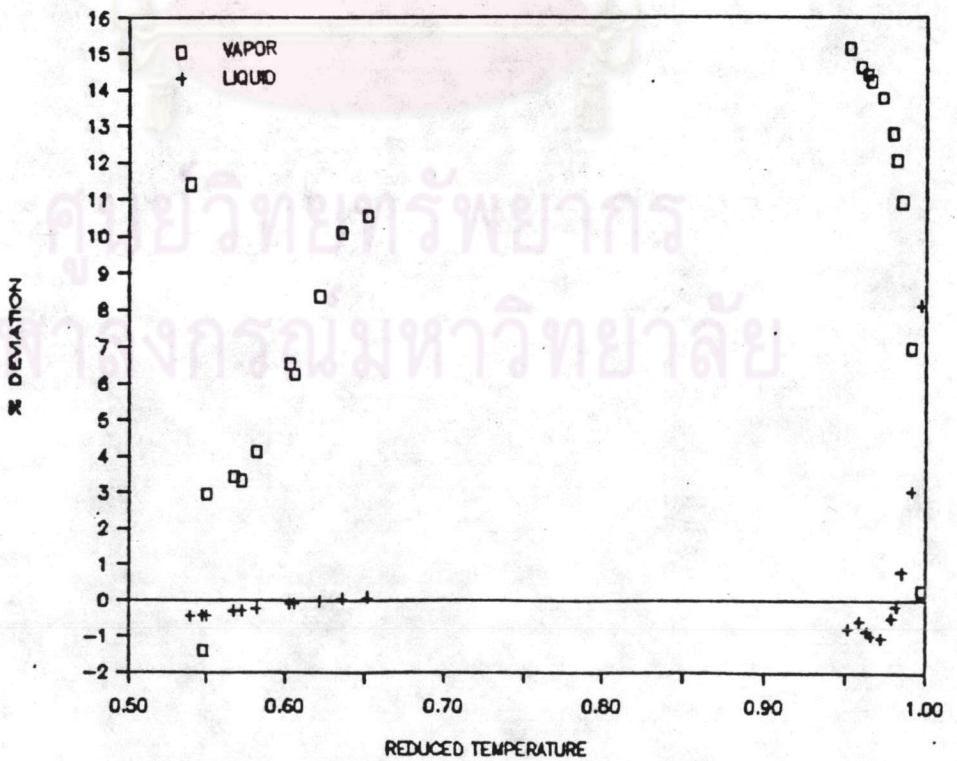

Figure 4.62 % Deviation in Saturated Volume for Ethane (calculated by Equation (3.34)).

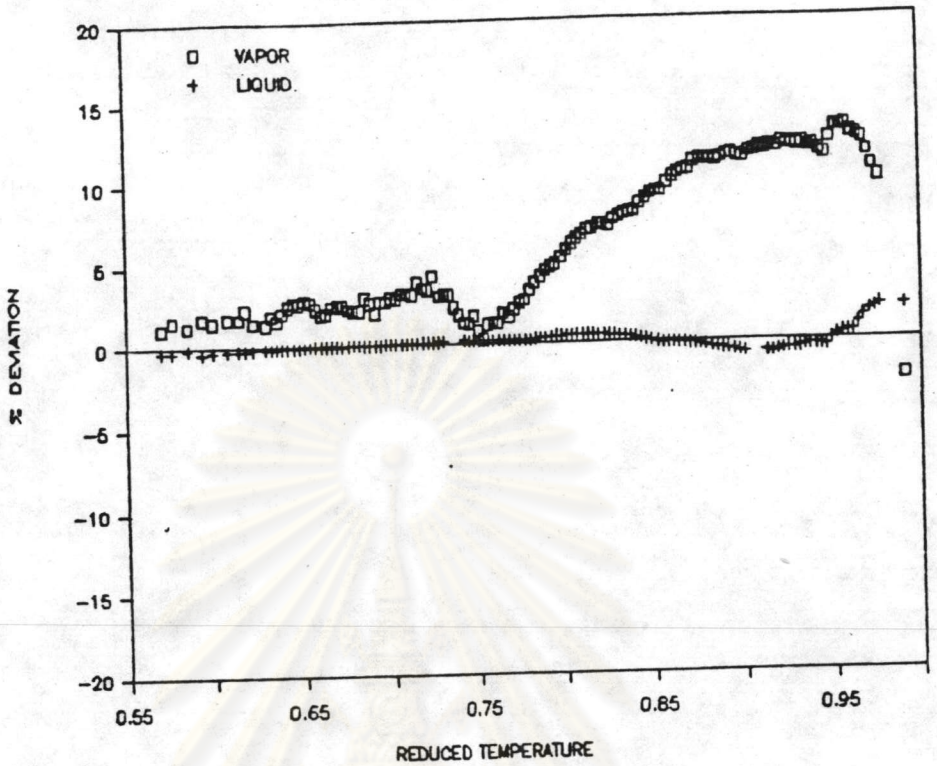

Figure 4.63 % Deviation in Saturated Volume for Propane (calculated by Equation (3.34)).

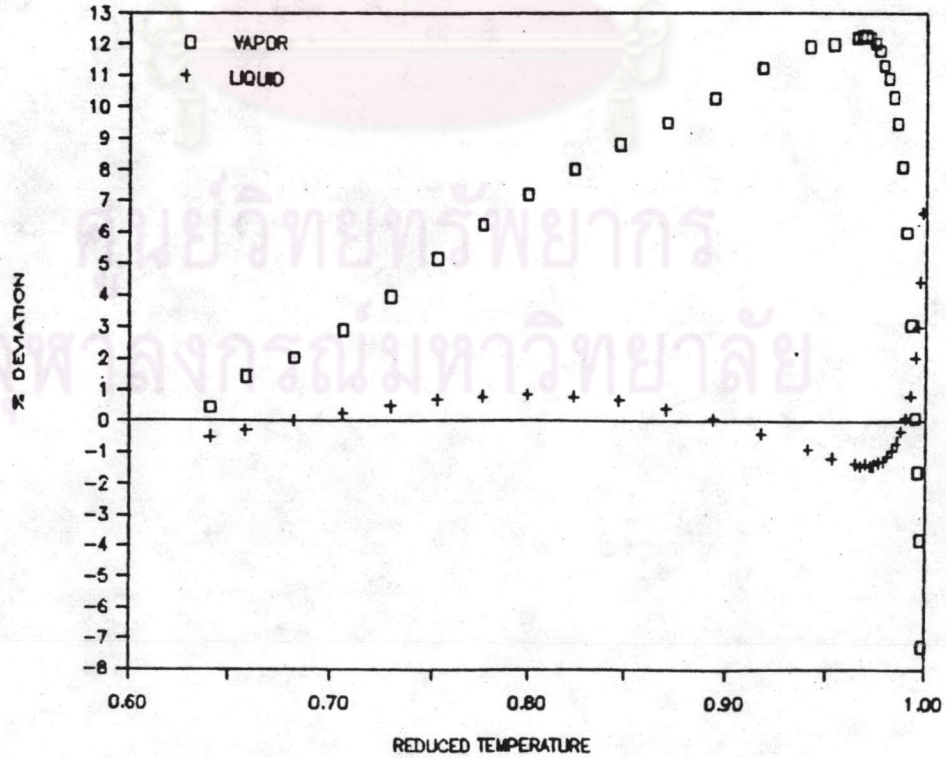

Figure 4.64 % Deviation in Saturated Volume for n-Butane (calculated by Equation (3.34)).

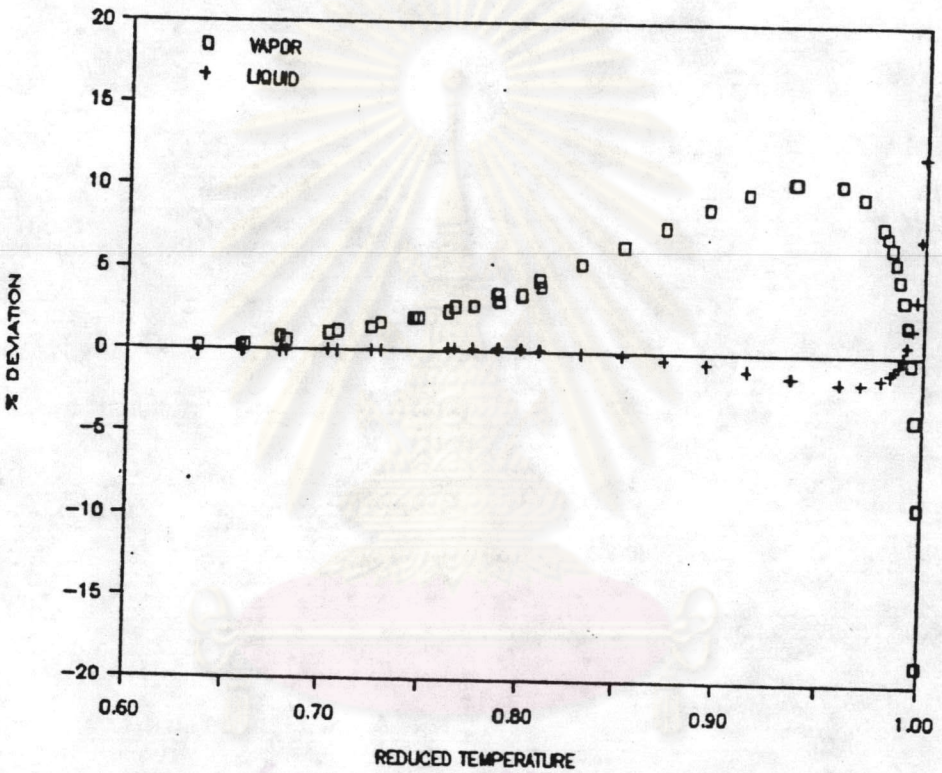

Figure 4.65 % Deviation in Saturated Volume for n-Pentane (calculated by Equation (3.34)).