

## Chapter Five

### Discussion

#### 5.1 Comparison of the Optimum $K_{ij}$ Values from Two Objective Functions

##### 5.1.1 CO<sub>2</sub> - Hydrocarbon Binaries

The mutual proximity of the  $K_{ij}$  values obtained from both methods for CO<sub>2</sub> systems can be examined in Table 4.1 and 4.2. Obviously, in all cases, the values from the bubble point pressure method yield better results in the AAD in bubble point pressure and vapor phase composition calculations. From the comparison, in all EOSs, the differences in  $K_{ij}$  values between the two tables do not exceed the limit of 0.0200 for binaries of CO<sub>2</sub> and light hydrocarbon upto i-butane. In addition, their effect on the accuracy of the bubble pressure predictions gives the differences of percent AAD within the range of 1.5%. However, higher deviation of the  $K_{ij}$  values from two tables is found in the binaries of CO<sub>2</sub> and heavier hydrocarbons as for n-pentane to n-decane, especially in the PR and PT equations. The difference in  $K_{ij}$  values increases to its maximum at 0.13 and thus causes the %AAD to be much higher in Table 4.2.

To demonstrate their statistical relationship, the regression of the  $K_{ij}$  values from both methods is made for all four equations and the result of each equation is presented in Figure 5.1-5.4. In this analysis, the degree of relationship between two data sets may be measured by the values of R squared. It can be seen that both SRK and SW equations yield  $R^2$  over 92% and higher than PR and PT equations. However, the  $R^2$  of both PR and PT equations are still in the acceptable range at 90.3% and 89.7% respectively.

Another trend can also be observed in Table 5.1 which gives the comparison of the average values of  $K_{ij}$  predicted for all four equations of state from both criteria. In terms of the systems, the average  $K_{ij}$  values for  $\text{CO}_2$ -n-propane and for  $\text{CO}_2$ -i-butane systems as predicted by both criteria are in good agreement within the range of 0.0100 for the four equations. In terms of the equations, the  $K_{ij}$  values obtained from both criteria for the PT equations are more consistent than the values for the other equations. The differences are less than 0.0100 for most systems except the  $\text{CO}_2$ -n-decane binary.

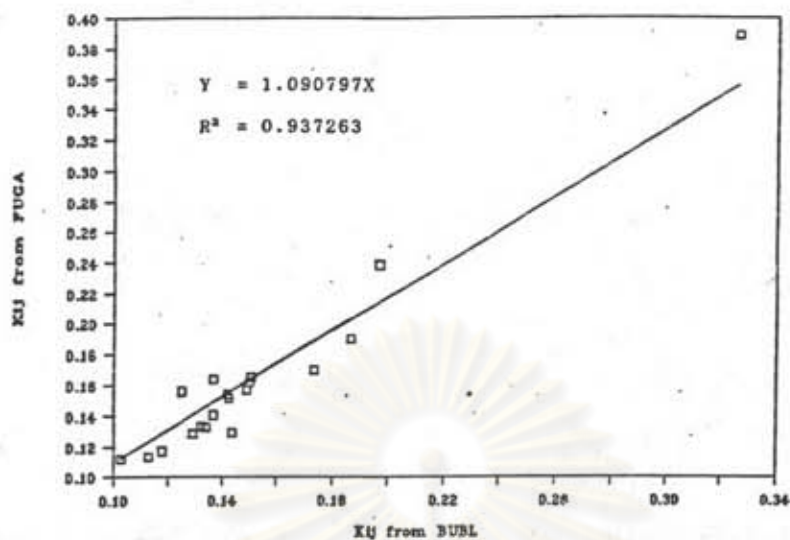


FIGURE 5.1 Regression results of the optimum  $K_{ij}$  values calculated by both criteria using SRK equation for  $\text{CO}_2$  systems

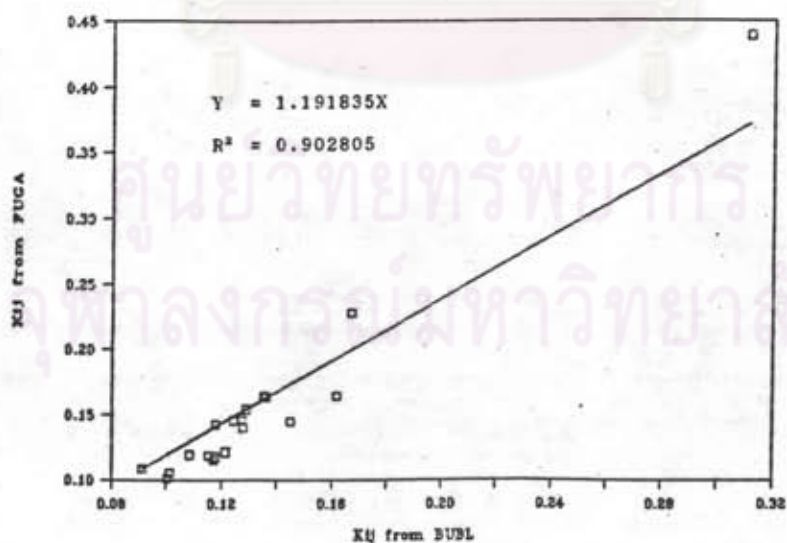


FIGURE 5.2 Regression results of the optimum  $K_{ij}$  values calculated by both criteria using PR equation for  $\text{CO}_2$  systems

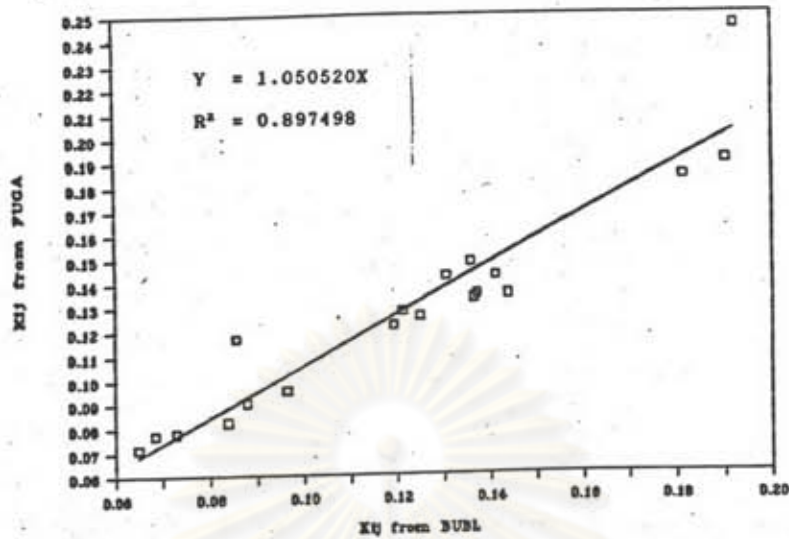


FIGURE 5.3 Regression results of the optimum  $K_{ij}$  values calculated by both criteria using PT equation for  $\text{CO}_2$  systems

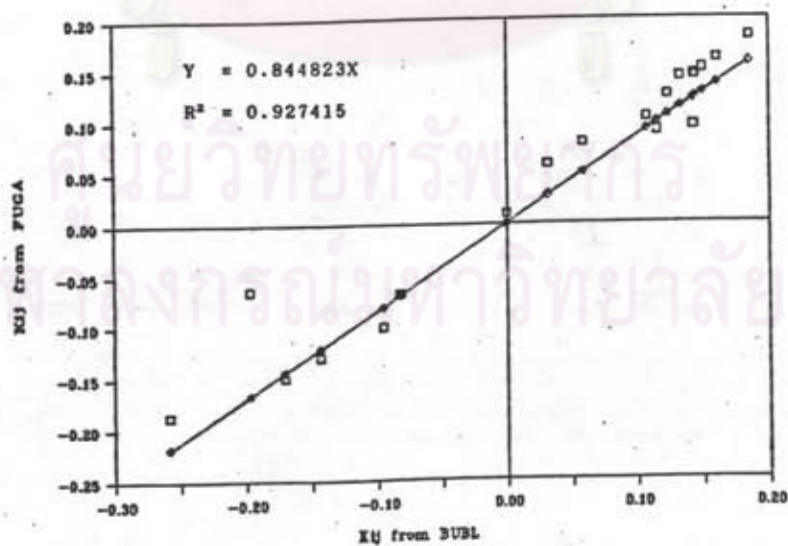


FIGURE 5.4 Regression results of the optimum  $K_{ij}$  values calculated by both criteria using SW equation for  $\text{CO}_2$  systems

TABLE 5.1 Comparison of the average values of the optimum  $K_{ij}$  from the Bubble point pressure criterion (1) and the Fugacity criterion (2) for CO<sub>2</sub> systems

System	SRK EOS		PR EOS		PT EOS		SW EOS	
	$K_{ij}$ from (1)	$K_{ij}$ from (2)	$K_{ij}$ from (1)	$K_{ij}$ from (2)	$K_{ij}$ from (1)	$K_{ij}$ from (2)	$K_{ij}$ from (1)	$K_{ij}$ from (2)
CO <sub>2</sub> - Ethane	0.1436	0.1291	0.1084	0.1192	0.1439	0.1338	0.1431	0.1301
CO <sub>2</sub> - n-Propane	0.1331	0.1330	0.1176	0.1167	0.1370	0.1333	0.1442	0.1437
CO <sub>2</sub> - i-Butane	0.1565	0.1574	0.1359	0.1373	0.1595	0.1597	0.1550	0.1544
CO <sub>2</sub> - n-Pentane	0.1431	0.1586	0.1269	0.1512	0.1269	0.1344	0.0972	0.0981
CO <sub>2</sub> - n-Heptane	0.1146	0.1246	0.1071	0.1200	0.0833	0.0848	-0.0275	-0.0197
CO <sub>2</sub> - n-Decane	0.2055	0.2366	0.1836	0.2380	0.1049	0.1292	-0.1919	-0.1324

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An important observation from these applications is that when the fugacity criterion is applied to find the optimum  $K_{ij}$  for a given EOS, the procedure is independent of the accuracy with which bubble pressure, composition or any other equilibrium variables is predicted. This is because all P-T-x-y data are introduced into the objective function. Therefore, this reason may explain why the accuracy of the  $K_{ij}$  predicted by this criterion is less than that predicted by the bubble point pressure criterion.

The only advantage of the fugacity criterion is that it requires much less computation time. The comparison is presented in Table 5.2 which the PT EOS is used as an example. It can be seen that the computing time requirement involved by the fugacity method is about ten times less than that used by the bubble point method. The reason for this is that this method can avoid iterations in objective function calculations. Therefore, in weighing between them, the accuracy must be sacrificed for the computation time and effort.

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TABLE 5.2 Comparison of the computation time required by both methods for CO<sub>2</sub>-n-hydrocarbon binaries with PT EOS

System	T (K)	N	Computation Time (min.)	
			Bubbl. Method	Fuga. Method
CO <sub>2</sub> -Ethane	250.00	13	87.0	7.0
CO <sub>2</sub> -n-Propane	266.49	11	75.4	6.6
CO <sub>2</sub> -i-Butane	344.27	5	40.5	4.2
CO <sub>2</sub> -n-Pentane	344.16	15	104.0	8.0
CO <sub>2</sub> -n-Heptane	310.66	23	150.5	12.4
CO <sub>2</sub> -n-Decane	462.56	4	38.5	4.0

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### 5.1.2 Methane - Heavier Hydrocarbon Binaries

From Table 4.3 and 4.4, the  $K_{ij}$  values of methane systems are much lower than those of  $\text{CO}_2$  systems and the proximity of  $K_{ij}$  values from two criteria is higher than that of  $\text{CO}_2$  systems. In all equations of state, the differences are found to be in the range of 0-0.0100 for every data set. Moreover, in some data sets where the  $K_{ij}$  values equal zero, both criteria give exactly the same value in most cases. An example for this indication can be observed in the methane-ethane binary. Therefore, when the regression of the  $K_{ij}$  values from both criteria is made, results from the SRK, PR, and SW equations show very high  $R$  squared values, especially for the SW equation. Only that obtained for the PT equation yields low  $R^2$  at 84.4%, as shown in Figure 5.5-5.8.

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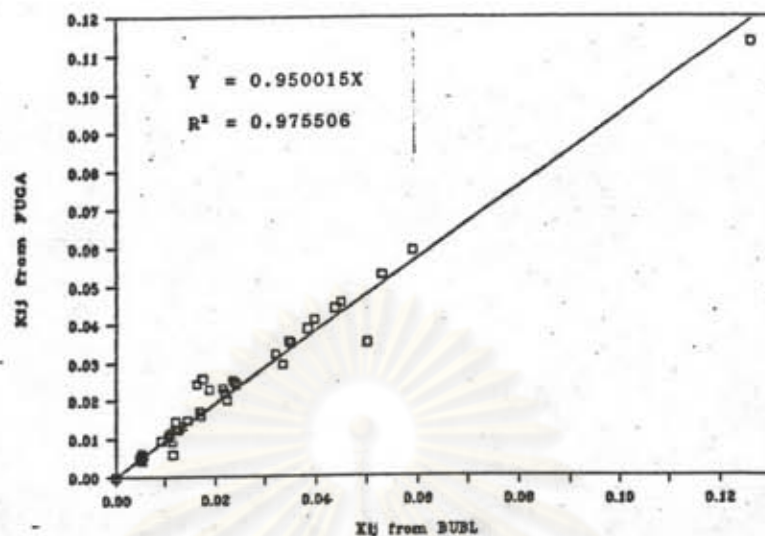


FIGURE 5.5 Regression results of the optimum  $K_{ij}$  values calculated by both criteria using SRK equation for methane systems

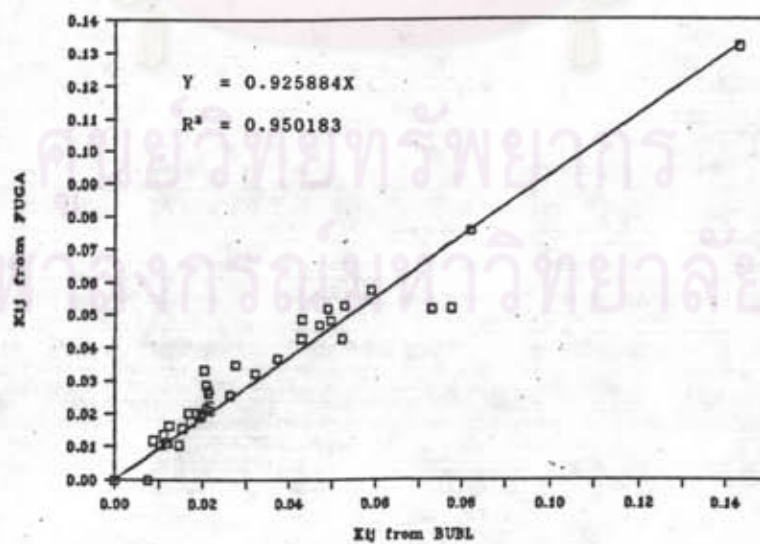


FIGURE 5.6 Regression results of the optimum  $K_{ij}$  values calculated by both criteria using PR equation for methane systems

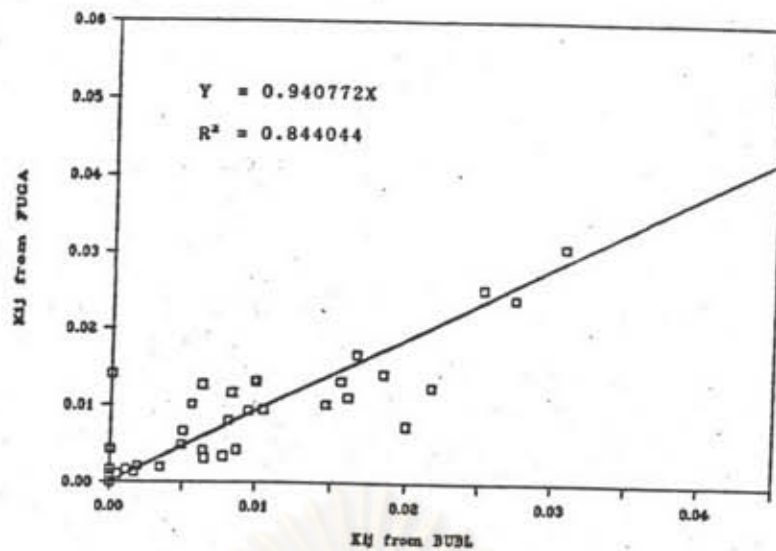


FIGURE 5.7 Regression results of the optimum  $K_{ij}$  values calculated by both criteria using PT equation for methane systems

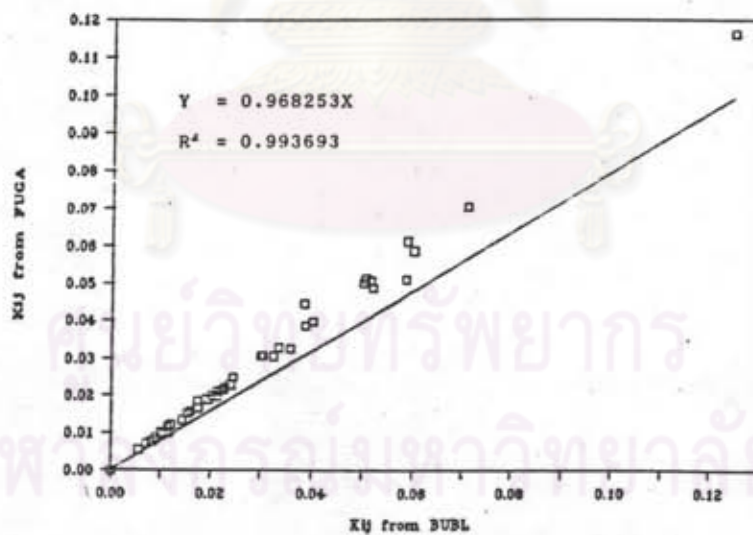


FIGURE 5.8 Regression results of the optimum  $K_{ij}$  values calculated by both criteria using SW equation for methane systems

In addition, the average values of  $K_{ij}$  for each methane binary in Table 5.3 show that both methods give acceptable average values for all four equations of state. The differences in all cases are less than 0.0050. When compared Table 5.3 with Table 5.1, it is also indicated that the closeness of the average  $K_{ij}$  values for methane systems is greater than that for  $\text{CO}_2$  systems.

Table 5.4 shows the comparison of computation time of both methods. In this case, the SW EOS is used as an example. The results are in the same manner as those described in previous section.



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TABLE 5.3 Comparison of the average values of the optimum  $K_{ij}$  from the Bubble point pressure criterion (1) and the Fugacity criterion (2) for Methane systems

System	SRK EOS		PR EOS		PT EOS		SW EOS	
	$K_{ij}$ from (1)	$K_{ij}$ from (2)	$K_{ij}$ from (1)	$K_{ij}$ from (2)	$K_{ij}$ from (1)	$K_{ij}$ from (2)	$K_{ij}$ from (1)	$K_{ij}$ from (2)
Methane - Ethane	0.0070	0.0069	0.0084	0.0090	0.0045	0.0051	0.0112	0.0112
Methane - n-Propane	0.0134	0.0141	0.0132	0.0150	0.0066	0.0089	0.0208	0.0206
Methane - n-Butane	0.0152	0.0160	0.0174	0.0208	0.0042	0.0055	0.0166	0.0162
Methane - n-Pentane	0.0182	0.0134	0.0238	0.0255	0.0056	0.0035	0.0204	0.0198
Methane - n-Hexane	0.0518	0.0495	0.0564	0.0603	0.0155	0.0130	0.0591	0.0568

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TABLE 5.4 Comparison of the computation time required by both methods for methane - heavier hydrocarbon binaries with SW EOS

System	T (K)	N	Computation Time (min.)	
			Bubbl. Method	Fuga. Method
Methane-Ethane	280.00	8	65.0	5.5
Methane-n-Propane	273.16	11	82.5	7.2
Methane-n-Butane	283.16	9	72.4	6.0
Methane-n-Pentane	273.17	10	80.5	7.1
Methane-n-Hexane	423.16	10	75.0	6.8

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### 5.1.3 Ethane - Heavier Hydrocarbon Binaries

The optimum  $K_{ij}$  values of ethane systems obtained from both methods were given in Table 4.5 and 4.6. From these tables, it can be seen that the  $K_{ij}$  values for most systems are equal to zero. In addition, good agreement of the  $K_{ij}$  values has been found since, as previously described, that if the  $K_{ij}$  equals zero, both methods normally yield the same value. Although in some data sets that the fugacity method does not give zero  $K_{ij}$  values while the bubble point method does, the differences are very small and the increment in deviations, at less than 0.08, is negligible. Only in the case of ethane-n-pentane binary at 410.94 K do all four equations have relatively high  $K_{ij}$  values. Still, acceptable values from both methods have been found.

Surprisingly, when the regression of the  $K_{ij}$  values from both methods is made for four equations, only the results from SRK and PT equations that give  $R^2$  higher than 95%, while the PR and SW equations yield relatively low  $R^2$  at 82.8% and 83.3% respectively, as indicated in Figure 5.9-5.12.

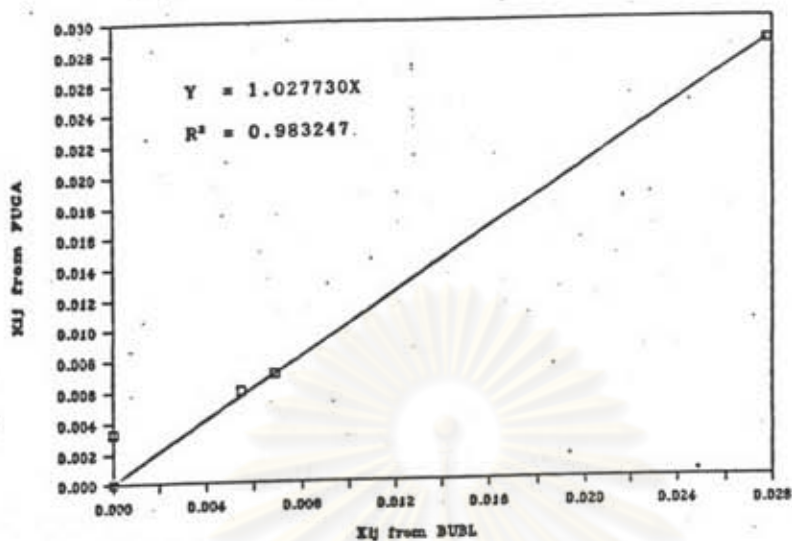


FIGURE 5.9 Regression results of the optimum  $K_{ij}$  values calculated by both criteria using SRK equation for ethane systems

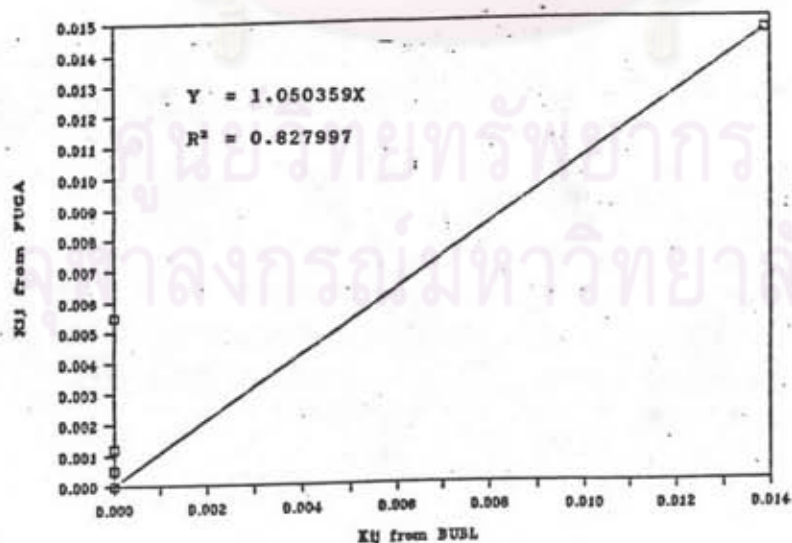


FIGURE 5.10 Regression results of the optimum  $K_{ij}$  values calculated by both criteria using PR equation for ethane systems

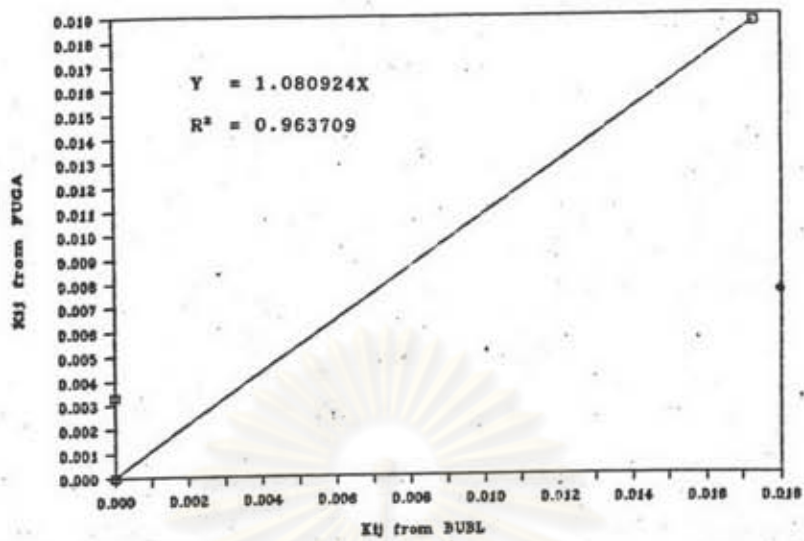


FIGURE 5.11 Regression results of the optimum  $K_{ij}$  values calculated by both criteria using PT equation for ethane systems

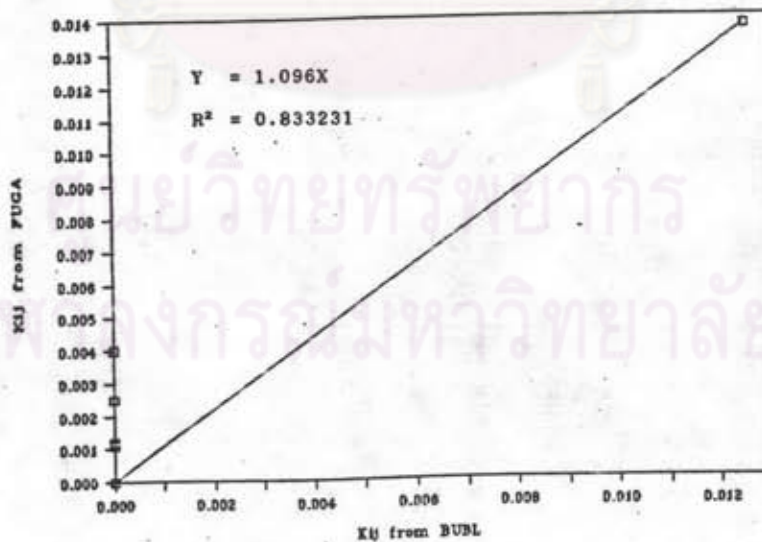


FIGURE 5.12 Regression results of the optimum  $K_{ij}$  values calculated by both criteria using SW equation for ethane systems



In Table 5.5 where the average  $K_{ij}$  values obtained from both methods are compared, good agreement between them is also found. The differences in all cases are less than 0.0020. In fact, the proximity of the average  $K_{ij}$  from both methods in this ethane systems are the highest among three systems studied.

Table 5.6 shows the computation time required by both methods for ethane systems using the SRK equation. The results are still the same. Therefore, this indicates that no matter which equation is used, the fugacity method will require computing times which are about ten times less than the computing times using the bubble point pressure method.

From these results, since it has been indicated that the  $K_{ij}$  values predicted from the bubble pressure criterion yield lower deviations, they will be used for further comparisons in the following sections.

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TABLE 5.5 Comparison of the average values of the optimum  $K_{ij}$  from the Bubble point pressure criterion (1) and the Fugacity criterion (2) for Ethane systems

System	SRK EOS		PR EOS		PT EOS		SW EOS	
	$K_{ij}$ from (1)	$K_{ij}$ from (2)	$K_{ij}$ from (1)	$K_{ij}$ from (2)	$K_{ij}$ from (1)	$K_{ij}$ from (2)	$K_{ij}$ from (1)	$K_{ij}$ from (2)
Ethane - n-Propane	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Ethane - i-Butane	0.0000	0.0017	0.0000	0.0003	0.0000	0.0000	0.0000	0.0020
Ethane - n-Pentane	0.0101	0.0104	0.0035	0.0053	0.0043	0.0055	0.0031	0.0046

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TABLE 5.6 Comparison of the computation time required by both methods for ethane - heavier hydrocarbon binaries with SRK EOS

System	T (K)	N	Computation Time (min.)	
			Bubbl. Method	Fuga. Method
Ethane-n-Propane	310.94	5	54.5	6.0
Ethane-i-Butane	311.27	5	60.5	7.5
Ethane-n-Pentane	410.94	6	62.5	7.8

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## 5.2 Significance of $K_{ij}$ in VLE Calculation

The absolute average percent deviation (AAD) in predicted bubble point pressures using four equations of state with and without  $K_{ij}$  are given in Table 5.7 for  $\text{CO}_2$  systems and in Table 5.8 for methane systems. In both cases, the average values of  $K_{ij}$  from the bubble point pressure criterion from previous section are used.

The results are very similar for all equations. Evidently, the incorporation of the optimum  $K_{ij}$  into the mixing rules of each equation of state increases the accuracy of the predicted bubble pressure values, especially for the  $\text{CO}_2$  systems. The AADs between the experimental and predicted values of every pair decrease dramatically from over 15% to less than 5% in almost all data sets. As an example of the accuracy improvement, Figure 5.13 gives the comparison of the VLE calculation of  $\text{CO}_2$ -n-propane binary at 244.27 K with and without the optimum  $K_{ij}$  using PT equation.

Therefore, for  $\text{CO}_2$  systems where the  $K_{ij}$  values are over 0.1, this coefficient cannot be neglected in performing the VLE calculations no matter which equation is used.

TABLE 5.7 Comparison of the deviation in bubble point pressure calculations with and without  $K_{ij}$  using four equations of state for CO<sub>2</sub> systems

System	T (K)	Range of P (ata)	N	SRK EOS		PR EOS		PT EOS		SW EOS	
				RAD(%) with $K_{ij}$	RAD(%) without $K_{ij}$	RAD(%) with $K_{ij}$	RAD(%) without $K_{ij}$	RAD(%) with $K_{ij}$	RAD(%) without $K_{ij}$	RAD(%) with $K_{ij}$	RAD(%) without $K_{ij}$
CO <sub>2</sub> - Ethane	250.00	14.23-18.51	13	Kij = .1436		Kij = .1084		Kij = .1439		Kij = .1431	
				0.39	18.86	1.03	17.61	0.52	19.07	1.89	18.44
CO <sub>2</sub> - n-Propane	266.49	7.96-25.79	11	Kij = .1331		Kij = .1176		Kij = .1370		Kij = .1442	
				2.08	20.11	2.09	22.56	1.88	20.31	1.94	17.52
CO <sub>2</sub> - i-Butane	310.94	7.14-70.90	8	Kij = .1565		Kij = .1359		Kij = .1595		Kij = .1550	
				1.24	14.77	1.24	16.54	1.87	22.14	1.84	14.67
				0.85	12.04	0.65	12.31	0.89	18.64	1.12	15.30
				2.37	18.34	1.74	19.97	2.01	24.67	2.09	20.43
CO <sub>2</sub> - n-Pentane	277.66	2.25-37.01	10	Kij = .1431		Kij = .1269		Kij = .1269		Kij = .0972	
				5.54	27.81	6.94	28.64	5.05	27.31	7.48	24.10
				3.48	25.09	4.62	24.97	4.52	21.87	5.37	22.65
				2.46	20.33	2.51	22.64	3.75	24.53	10.26	25.16
CO <sub>2</sub> - n-Heptane	310.66	1.84- 74.64	23	Kij = .1146		Kij = .1071		Kij = .0833		Kij = -.0275	
				2.23	17.90	3.09	16.87	2.46	15.21	8.45	16.42
				0.88	11.07	1.31	12.05	1.19	13.27	9.24	8.13
				1.89	15.66	2.94	17.94	1.77	15.64	6.85	15.34
CO <sub>2</sub> - n-Decane	462.56	19.36-50.70	4	Kij = .2055		Kij = .1836		Kij = .1049		Kij = -.1919	
				1.67	16.64	1.56	17.27	1.48	14.30	2.26	18.52
				1.45	17.04	1.87	18.17	1.49	12.58	1.56	19.64
				1.61	19.38	2.29	20.08	1.52	18.54	1.89	22.45
CO <sub>2</sub> - n-Decane	583.66	19.76-50.40	4	2.14	27.00	5.46	28.83	2.46	24.06	1.85	21.30

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TABLE 5.8 Comparison of the deviations in bubble point pressure calculations with and without  $K_{ij}$  using four equations of state for Methane systems

System	T (K)	Range of P (ata)	N	SRK EOS		PR EOS		PT EOS		SW EOS	
				ARD(%) with $K_{ij}$	ARD(%) without $K_{ij}$	ARD(%) with $K_{ij}$	ARD(%) without $K_{ij}$	ARD(%) with $K_{ij}$	ARD(%) without $K_{ij}$	ARD(%) with $K_{ij}$	ARD(%) without $K_{ij}$
Methane - Ethane				Kij = .0070		Kij = .0084		Kij = .0045		Kij = .0112	
	280.00	28.50-62.10	8	3.21	3.47	3.21	3.01	1.83	2.03	2.49	2.67
	270.00	22.53-60.22	9	2.04	2.17	4.41	4.68	0.74	0.79	2.23	2.75
	260.00	17.80-65.18	11	1.46	2.05	4.37	4.52	0.76	0.79	2.24	2.68
	199.93	3.62-50.35	11	2.91	2.82	3.27	3.12	2.97	2.93	3.62	3.44
	192.40	2.65-46.40	8	2.32	2.29	3.89	3.72	2.34	2.29	3.71	3.58
	190.85	2.69-45.60	8	1.17	1.06	2.64	2.52	1.16	1.07	2.35	2.11
	189.66	2.44-43.15	9	1.35	1.24	3.24	3.18	1.76	1.68	2.98	2.75
	186.12	2.50-38.65	11	1.18	1.08	4.37	4.28	1.29	1.21	3.34	3.22
	172.05	2.10-23.05	9	1.97	1.85	3.71	3.64	1.77	1.72	1.86	1.71
	158.16	1.76-13.55	10	3.51	3.39	5.75	5.51	3.51	3.45	3.47	3.38
	144.27	1.86- 6.67	7	0.79	0.85	2.84	2.62	0.73	0.68	1.89	1.86
	130.38	1.91- 3.31	4	1.43	1.86	5.30	5.11	1.46	1.49	3.68	3.79
Methane - n-Propane				Kij = .0134		Kij = .0132		Kij = .0066		Kij = .0208	
	273.16	6.80-95.26	11	4.58	6.77	3.66	6.42	1.85	3.89	2.91	9.64
	256.49	6.80-88.45	13	2.57	1.79	1.11	4.87	1.23	1.32	1.98	5.45
	241.49	6.80-88.45	13	1.56	2.26	1.63	5.64	1.34	1.60	2.55	8.16
	226.49	6.80-74.84	8	3.68	5.79	5.10	9.13	3.86	5.05	3.98	10.98
	213.72	1.87-63.90	10	1.75	1.49	2.88	3.40	1.44	1.25	2.44	7.32
	195.16	2.08-48.20	13	1.49	1.76	2.51	5.20	2.34	4.50	3.19	5.88
	192.26	2.04-45.85	10	1.88	1.53	2.21	4.88	1.89	1.62	2.57	4.79
	187.55	2.79-39.85	9	1.52	2.41	2.76	6.01	1.85	2.01	2.64	5.03
	172.05	2.10-23.25	8	6.08	8.88	5.44	11.81	2.88	4.44	3.47	11.62
	158.16	1.70-13.70	8	6.24	8.64	3.89	9.98	3.03	4.88	2.63	8.70
	144.27	2.11- 7.35	6	2.79	6.02	6.31	5.20	2.56	3.33	3.21	8.61
	130.38	1.84- 2.86	3	1.81	5.43	2.76	2.20	1.32	2.81	3.41	2.34
Methane - n-Butane				Kij = .0152		Kij = .0174		Kij = .0042		Kij = .0166	
	283.16	3.47- 95.26	9	1.57	5.89	2.31	3.32	1.35	1.27	3.04	6.72
	255.36	1.36-108.66	9	6.44	10.92	3.76	5.98	3.91	3.80	3.87	7.09
	227.56	3.40- 81.44	8	4.35	8.62	4.60	5.66	4.03	3.88	3.65	7.03
	210.96	1.36- 66.20	10	4.31	2.45	3.89	4.87	3.86	3.43	3.42	3.41
	194.11	1.36- 46.06	9	4.75	3.31	3.88	5.78	2.46	2.43	3.98	6.24
	185.96	1.36- 37.35	9	5.01	7.49	4.21	7.61	2.48	2.56	4.03	7.80
	177.56	1.36- 27.49	8	1.58	5.72	2.94	7.01	1.25	1.46	2.37	7.32
	166.46	1.36- 19.26	8	4.67	7.83	3.23	8.13	2.06	2.31	3.08	6.97

TABLE 5.8 (Continued)

System	T (K)	Range of P (atm)	N	SRK EOS		PR EOS		PT EOS		SW EOS	
				ARD(%) with Kij	ARD(%) without Kij	ARD(%) with Kij	ARD(%) without Kij	ARD(%) with Kij	ARD(%) without Kij	ARD(%) with Kij	ARD(%) without Kij
Methane - n-Pentane	273.17	13.62-136.09	10	Kij = .0182		Kij = .0238		Kij = .0056		Kij = .0204	
	248.35	6.82-122.48	10	6.49	9.93	7.31	10.03	6.37	7.08	6.78	12.28
	223.93	6.82- 81.65	7	3.94	6.22	3.86	7.68	4.21	3.99	5.74	10.20
	199.87	3.42- 40.83	5	8.66	7.83	7.65	8.98	9.81	9.29	8.01	11.94
	194.18	6.81- 40.83	4	7.30	6.54	6.54	8.31	7.32	7.00	9.94	10.21
	192.64	6.82- 40.83	4	6.21	8.66	5.68	7.76	5.99	5.80	8.64	12.26
	176.22	1.37- 20.43	6	6.45	9.21	4.78	11.20	5.97	7.04	5.41	9.87
Methane - n-Hexane				Kij = .0518		Kij = .0564		Kij = .0155		Kij = .0591	
	423.16	10.00-100.00	10	2.78	11.20	2.54	12.30	3.03	5.96	5.67	16.84
	373.16	10.00-100.00	10	0.67	5.61	0.89	6.07	1.61	1.54	1.78	8.67
	348.16	10.00-100.00	10	0.34	4.97	0.28	3.21	0.74	0.59	1.21	5.20
	323.16	10.00-100.00	10	0.60	6.31	0.41	3.11	1.10	0.50	0.88	4.89
	298.16	10.00-100.00	10	0.79	6.80	0.64	4.46	1.35	0.92	1.02	5.61
	273.17	1.71-149.69	16	1.98	7.08	2.29	8.81	1.89	4.51	1.63	8.86
	248.15	1.37-159.01	17	5.11	12.34	5.11	11.20	4.03	7.02	3.79	13.54
	223.16	1.37-115.67	16	6.83	15.08	6.89	15.23	5.89	8.95	7.19	18.91
	210.16	1.37- 81.65	10	1.96	10.64	2.27	8.71	7.11	16.57	2.03	11.64
	198.06	1.35- 68.04	10	1.69	9.61	1.29	7.45	6.67	15.31	1.43	8.12

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In methane mixtures, since the  $K_{ij}$  values are less than those in  $\text{CO}_2$  mixtures, their effect in the VLE prediction accuracy is not so meaningful, especially for methane-light hydrocarbon binaries at low to medium temperature. In the case of methane-n-pentane and methane-n-hexane binaries, the accuracy improvement effect of the  $K_{ij}$  has increased significantly for all equations. For PT equation, even though the  $K_{ij}$  values are still low for these two binaries, its effect has become in the same level as the other equations. In fact, the  $K_{ij}$  values predicted by PT EOS are the lowest among those equations in every mixture and temperature. Figure 5.14 indicates the accuracy effect of VLE calculation with and without the optimum  $K_{ij}$  of the PT equation for methane-n-pentane system at 273.17 K.

One drawback of using the average  $K_{ij}$  values in the VLE calculation can be seen in these systems. In case of zero or very low  $K_{ij}$  with minimum deviations in some data sets, especially in methane-ethane and methane-n-propane binaries, using the average values in the calculations will give higher deviations since the average values in these cases are remarkably different from the optimum values.



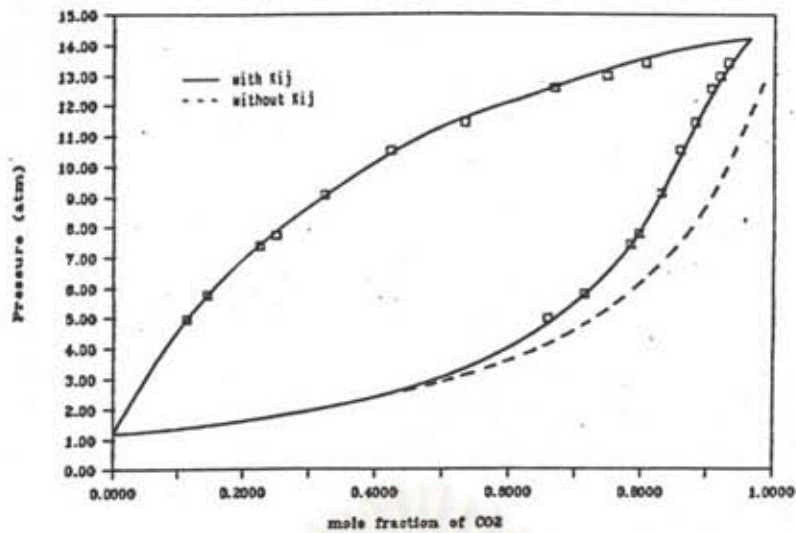


FIGURE 5.13 Comparison of the VLE results calculated with and without  $K_{ij}$  for  $\text{CO}_2$ -n-Propane binary at 244.27 K using PT equation

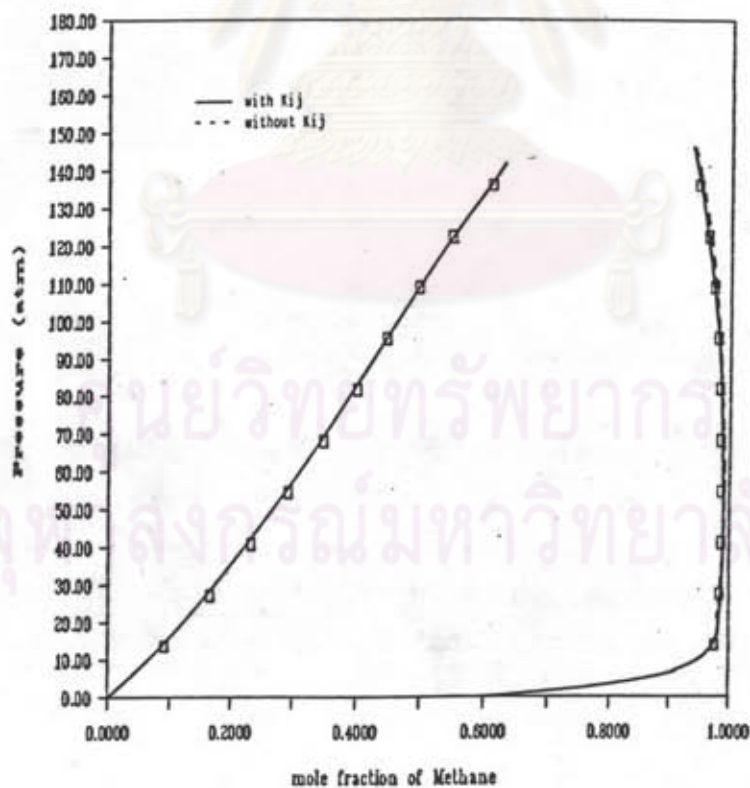


FIGURE 5.14 Comparison of the VLE results calculated with and without  $K_{ij}$  for Methane-n-Pentane binary at 273.17 K using PT equation

This comparison has not been made for ethane systems since most binaries have  $K_{ij}$  equal to zero. Therefore, in contrast to the previous two mixtures, the VLE calculation for these systems may be performed accurately without the  $K_{ij}$ . The only exception is for ethane-n-pentane binary at high temperature of 410.94 K which their  $K_{ij}$  values are relatively high when compared to other binaries. When the VLE predictions are made for this binary without  $K_{ij}$  using each equation, the results are in the same manner as methane-heavy hydrocarbon systems. The %AADs increase from 1.19 to 2.78 for SRK EOS, 2.09 to 2.98 for PR EOS, 1.17 to 1.95 for PT EOS, and 1.61 to 2.34 for SW EOS.



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### 5.3 Comparison of Four Equations of State for Vapor-Liquid Equilibrium Calculations

Vapor-liquid equilibrium calculation has been performed using the predicted optimum binary interaction coefficients. The details of average absolute deviations (AAD) in bubble point calculations has been shown in Table 4.1 for CO<sub>2</sub> systems, in Table 4.3 for methane systems, and in Table 4.5 for ethane systems. In addition, a summarized results of SW, PT EOS, and experimental data are also presented in Chapter 4. In this section, the comparison of the four equations is made through the total average of the AAD for each binary system.

#### 5.3.1 CO<sub>2</sub> - Hydrocarbon Binaries

Table 5.9 presents the total AAD between experimental and predicted bubble pressure as calculated by four equations for CO<sub>2</sub>-hydrocarbons. In overall, the SRK equations seems to work better than the other three for CO<sub>2</sub> systems. The performance of the PT equation is also close to that of the SRK equation. Both of them give the AAD less than 2% for most systems, except for CO<sub>2</sub>-n-pentane which the predicted results are inferior in all equations. Yet, the PR and SW equations do not perform very well in overall predictions. They give much higher deviations than those two equations, especially for CO<sub>2</sub>-heavy hydrocarbons.

TABLE 5.9 Total deviations between experimental and predicted bubble pressure for CO<sub>2</sub> systems

System	N	SRK	PR	SW	PT
CO <sub>2</sub> -Ethane	13	0.39	1.03	1.89	0.53
CO <sub>2</sub> -n-Propane	21	1.93	2.38	1.63	1.50
CO <sub>2</sub> -i-Butane	21	1.11	1.10	1.66	1.17
CO <sub>2</sub> -n-Pentane	48	3.35	4.24	5.98	3.59
CO <sub>2</sub> -n-Heptane	63	1.35	2.31	5.29	1.76
CO <sub>2</sub> -n-Decane	16	1.35	1.99	1.38	1.28
Overall	182	1.58	2.18	2.97	1.64

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The comparisons between experimental and predicted bubble point pressures by the PT and SW equations in Figure 4.1 to 4.6 also showed the preferable performance of the PT equation over the SW equation. In addition, the comparison of all four equations for CO<sub>2</sub>-n-propane at 266.49 K is given in Figure 5.15.

### 5.3.2 Methane - Heavier Hydrocarbon Binaries

The results from the bubble point pressure calculations of methane systems using four equations have drawn the same conclusion as the results of CO<sub>2</sub> systems. From Table 5.10, in overall, the PT and SRK equations yield better results than the PR and SW equations. However, the performance of all equations is not significantly distinct. The four equations produce the AAD within the range of 3.0% except for methane-ethane binary using PR equation and methane-n-pentane system by all equations which poor results are obtained.

The superior performance of the PT equation over the SW equation can be observed in Figure 4.7-4.11 which shows the comparison between the experimental and calculated bubble pressures for both equation. Figure 5.16 also shows the bubble pressure calculations for methane-propane binary at 273.16 k using all four equations.

TABLE 5.10 Total deviations between experimental and predicted bubble pressure for methane systems

System	N	SRK	PR	SW	PT
Methane-Ethane	105	1.69	3.58	2.58	1.56
Methane-n-Propane	112	2.31	2.57	2.41	1.79
Methane-n-Butane	70	2.67	3.14	2.45	2.87
Methane-n-Pentane	46	5.14	4.72	5.98	5.63
Methane-n-Hexane	119	1.87	2.04	2.24	1.75
Overall	452	2.74	3.21	3.13	2.68

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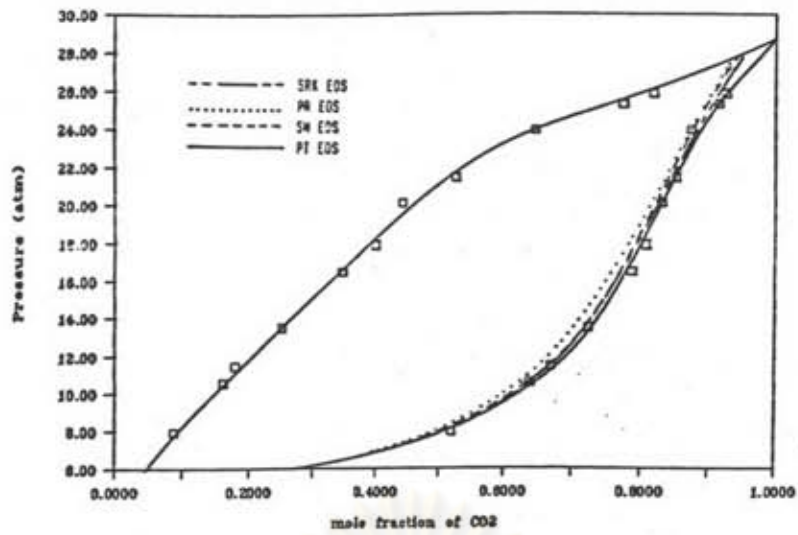


FIGURE 5.15 Comparison of the VLE calculations for  $\text{CO}_2$ -  
n-Propane mixture at 266.49 K using four  
equations of state

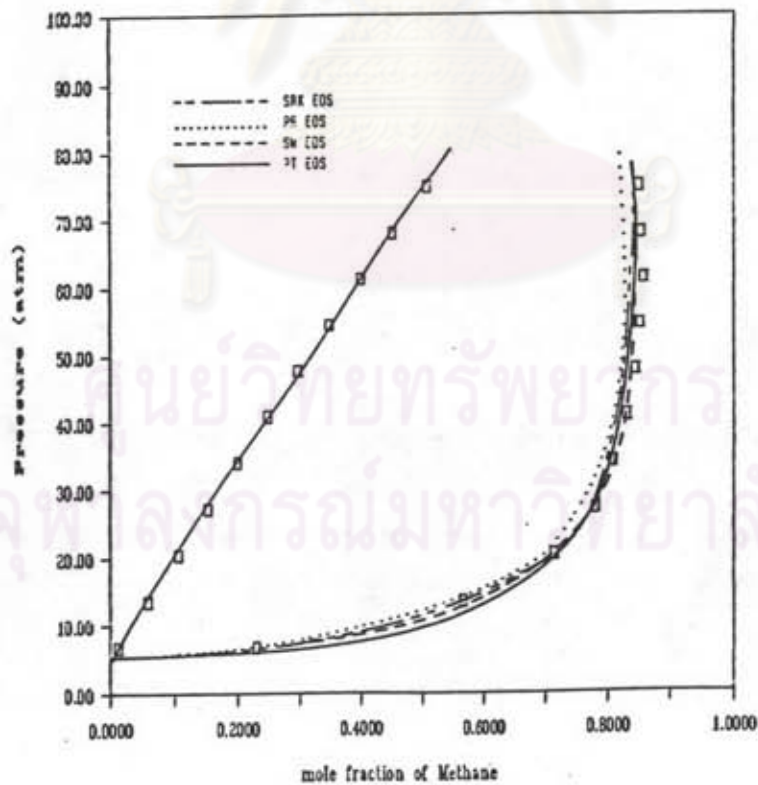


FIGURE 5.16 Comparison of the VLE calculations for Methane-  
n-Propane mixture at 276.16 K using four  
equations of state

### 5.3.3 Ethane - Heavier Hydrocarbon Binaries

Table 5.11 gives the total deviations in bubble point pressure calculations for ethane systems using all four equations. In this case, the PT and SRK equation are still in superior performance than the other two. However, the SW and PR equations also give the acceptable results in these binaries. Only for ethane-i-butane binary that the PR equation does not perform well and this causes the overall deviation of this equation to be higher than 2.00%.

Again, refer to Figure 4.12 -4.14 in Chapter Four, the comparison between experimental and calculated bubble pressure by The PT and SW equations has been given. Figure 5.17, as an example, presents the comparison of all four equations for ethane-i-butane binary at 311.27 K.

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TABLE 5.11 Total deviations between experimental and predicted bubble pressure for ethane systems

System	N	SRK	PR	SW	PT
Ethane-n-Propane	9	1.18	1.62	1.13	0.70
Ethane-i-Butane	10	1.90	3.84	2.19	1.77
Ethane-n-Pentane	22	1.04	1.48	2.00	1.18
Overall	41	1.37	2.31	1.77	1.22

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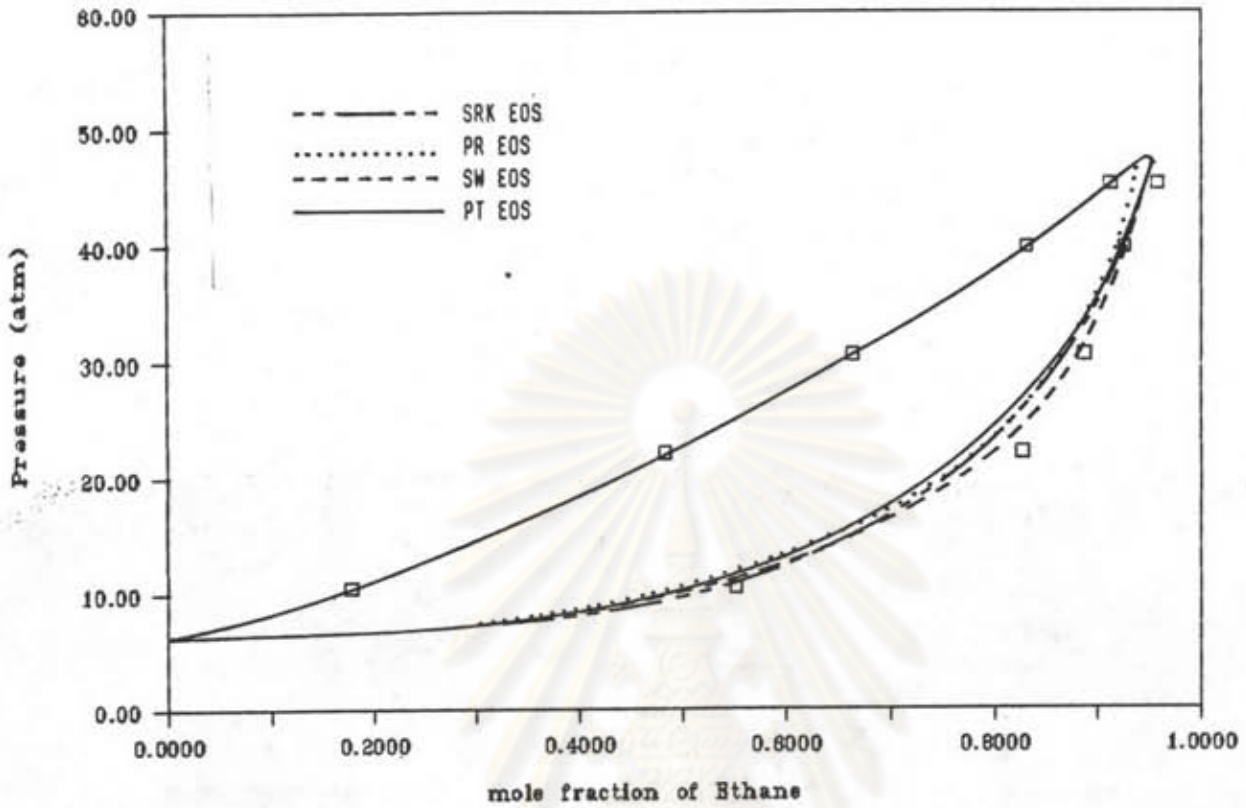


FIGURE 5.17 Comparison of the VLE calculations for Ethane-i-Butane mixture at 311.27 K using four equations of state

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## 5.4 Comparison of the Optimum $K_{ij}$ Values for the SRK and PR Equations of State with Earlier Works

### 5.4.1 The SRK Equation

Graboski and Daubert (16), in 1978, have reported an extensive tabulation of the binary interaction coefficients for mixtures containing nonhydrocarbon components with hydrocarbons using the SRK equation. In their work, they also employed the minimization of the bubble point pressure deviations. Unfortunately, they assumed the  $K_{ij}$  value to be a universal constant for a given binary pair and be independent of temperature and pressure. In addition, the search optimization routine was that of the least square method.

Reevaluation of their procedure in search of the optimum  $K_{ij}$  for VLE calculations with the SRK equation was presented by Eillott and Daubert (43) in 1985. They used the same objective function but changed to a larger data base which resulted in slight improvements for the previous one.

Comparison of the  $K_{ij}$  values for the SRK equation obtained in this work and from those works are given in Table 5.12. The optimum  $K_{ij}$  values here are in good agreement with those of Eillott and Daubert. The

differences between these two are less than 0.01. On the other hand, when compared with the values from Graboski and Daubert's work, they seem to have no relationship to each other. This may be due to the data base used in each work and the optimization technique employed. Another distinction is that, in this work, the optimum  $K_{ij}$  are evaluated depending on each temperature and pressure which seems to be more accepted by many investigators.

#### 5.4.2 The PR Equation

Kato et al. (44) studied several  $\text{CO}_2$ -hydrocarbon systems and expressed  $K_{ij}$  in the PR equation as a function of the temperature and of the acentric factor of the solvent. In their work, they obtained the  $K_{ij}$  values by regression analysis of experimental data using the bubble point pressure objective function.

Table 5.13 give the  $K_{ij}$  values found in this work and those proposed by Kato et al. for  $\text{CO}_2$  systems. The comparison indicates that no agreement has been found between these two works. Among six systems, only  $\text{CO}_2$ -n-Pentane binary yields acceptable values between the two. The explanation for this result may be the different data base employed and different algorithm used in calculation method. From this application, as an example, the algorithm

TABLE 5.12  $K_{ij}$  values in the SRK equation as predicted by Graboski and Daubert (16), by Eillott and Daubert (43), and in this work for CO<sub>2</sub> systems

System	$K_{ij}$		
	this work	Graboski & Daubert	Eillott & Daubert
CO <sub>2</sub> -Ethane	0.1436	0.1346	0.1340
CO <sub>2</sub> -n-Propane	0.1331	0.1018	0.1280
CO <sub>2</sub> -i-Butane	0.1565	0.1474	-
CO <sub>2</sub> -n-Pentane	0.1431	0.1278	0.1407
CO <sub>2</sub> -n-Heptane	0.1146	0.1136	0.1120
CO <sub>2</sub> -n-Decane	0.2055	0.1377	-

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TABLE 5.13  $K_{ij}$  values in the PR equation as predicted by Kato et al. (44) and in this work for CO<sub>2</sub> systems

System	$K_{ij}$	
	this work	Kato et al.
CO <sub>2</sub> -Ethane	0.1084	0.1365
CO <sub>2</sub> -n-Propane	0.1176	0.1318
CO <sub>2</sub> -i-Butane	0.1359	0.1275
CO <sub>2</sub> -n-Pentane	0.1269	0.1271
CO <sub>2</sub> -n-Heptane	0.1071	0.1483
CO <sub>2</sub> -n-Decane	0.1836	0.1585

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of the program revealed some effects on the results obtained.



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