CHAPTER IV

RESULTS AND DISCUSSION

Results of a series of calculated investigation of thirteen binary mixtures are reported: T, P, x data of vapor-liquid equilibria (VLE), H^E, T, x data of calorimetric measurements. A summary of the binary mixtures is given in Table 4.1.

Table 4.1 Studied binary systems.

Systems (1 + 2)	Literature source	
	VLE	H^E
benzene + cyclohexane	Kurihara et al., (1997)	Hsu and Clever (1975) Kuus et al., (1996) Meyer et al., (1977) Stokes et al., (1969)
butanenitrile + 2-butanol	Garriga et al., (1997)	
1-chloropentane + di-n-butyl ether	Paul et al., (1986)	
1-chlorohexane + ethylbenzene	Paul et al., (1988)	
1-chlorohexane + n-propylbenzene	Paul et al., (1988)	
1,2-dichloroethane + di-n-butyl ether	Paul et al., (1986)	
1,2-epoxybutane + ethanol	Comelli and Francesconi (1996)	
1,2-epoxybutane + methanol	Comelli and Francesconi (1996)	
1,2-epoxybutane + 2-propanol	Comelli and Francesconi (1996)	
ethyl formate + benzene	Ohta and Nagata (1980)	
ethyl formate + cyclohexane	Ohta and Nagata (1980)	
toluene + 1-chlorohexane	Paul et al., (1988)	
1,1,1-trichloroethane + di-n-butyl ether	Paul et al., (1986)	

Note: the experimental data are the literature values.

Table 4.2 Parameters and percent average absolute deviations ,%AAD (P) of Wilson and UNIQUAC equations using VLE data.

	Wilson			UNIQUAC		
T /K	λ_{12} J/mol	λ_{21} J/mol	%AAD (P)	u_{12} J/mol	u_{21} J/mol	%AAD (P)
Benzene (1) + Cyclohexane (2)						
323.15	939.22	293.13	0.15	-295.09	769.59	0.15
333.15	888.61	264.94	0.19	-398.85	870.58	0.19
1-Chloropentane (1) + Di-n-butyl ether (2)						
313.15	1800.51	-1566.16	0.25	-630.59	782.87	0.24
323.15	1491.71	-1327.61	0.12	-522.17	644.74	0.13
1,2-Dichloroethane (1) + Di-n-butyl ether(2)						
330.00	596.75	1755.14	1.06	715.57	-176.50	1.09
350.00	911.50	852.32	0.34	161.26	320.73	0.35
370.00	894.01	660.04	0.58	81.79	364.10	0.58
1,1,1-Trichloroethane (1) + Di-n-butyl ether(2)						
323.15	5843.38	-3966.59	1.28	-1276.74	1695.95	1.21
343.15	-1275.74	3448.77	1.21	2222.41	-1566.11	1.22
Toluene (1) + 1-Chlorohexane (2)						
323.15	1967.51	-1892.02	0.19	1938.62	-1502.32	0.16
343.15	-1141.53	1786.36	0.12	1977.11	-1546.21	0.12
1-Chlorohexane (1) + Ethylbenzene (2)						
323.15	-178.33	60.67	0.06	183.88	-270.68	0.06
343.15	1435.73	-1069.28	0.03	-1323.45	1612.69	0.03
1-Chlorohexane (1) + n-Propylbenzene (2)						
363.15	1845.66	-1391.74	0.36	-1290.06	1572.15	0.36
1,2-Epoxybutane (1) + Methanol (2)						
298.15	-289.85	4207.66	0.43	2890.63	-363.19	0.50
1,2-Epoxybutane (1) + Ethanol (2)						
298.15	-60.08	3592.12	0.46	2089.98	-432.79	0.58

Table 4.2 (continued)

T /K	Wilson λ_{12} J/mol	Wilson λ_{21} J/mol	Wilson %AAD (P)	UNIQUAC u_{12} J/mol	UNIQUAC u_{21} J/mol	UNIQUAC %AAD (P)
1,2-Epoxybutane (1) + 2-Propanol (2)						
298.15	1079.17	1778.64	2.25	423.82	566.19	2.26
Ethyl formate (1) + Benzene (2)						
323.15	937.41	114.68	0.68	-329.60	520.70	0.68
Ethyl formate (1) + Cyclohexane (2)						
323.15	3859.97	991.66	1.81	-393.48	1985.95	1.76
Butanenitrile (1) + 2-Butanol (2)						
278.15	3390.15	1673.51	1.06	-30.50	1534.72	1.26
288.15	3213.75	1279.84	0.61	-177.36	1588.84	0.75
293.15	2933.45	1199.72	0.53	-163.20	1477.35	0.73
298.15	2853.62	1076.80	0.54	-210.31	1483.82	0.60
303.15	2747.78	1005.28	0.43	-223.00	1450.58	0.55
308.15	2583.45	993.87	0.37	-202.99	1377.38	0.46
313.15	2376.30	976.37	0.28	-171.62	1274.35	0.33
323.15	2129.93	883.28	0.34	-169.33	1172.08	0.36

4.1 Vapor-liquid equilibria

The experimental data were correlated by the Wilson (section 2.2.1), and UNIQUAC (section 2.2.2) equations. The values of binary parameters for each equation were determined with the Newton method.

The binary parameters for the correlation equations are shown in Table 4.2, along with the percentage average absolute deviations between the calculated and experimental pressures %AAD (P). Figure 4.1 shows a comparison between the experimental P-x data and the P-x curves calculated using the fitted Wilson and UNIQUAC parameters for the benzene + cyclohexane system. The same comparison is made in Figures 4.2 through 4.4 for the di-n-butyl ether with 1-chloropentane, 1,2-dichloroethane, and 1,1,1-trichloroethane systems, respectively. Figures 4.5 to 4.7 show the same comparisons for the 1-chlorohexane with three n-alkylbenzenes: toluene, ethylbenzene, and n-propylbenzene systems, respectively. For the butanenitrile + 2-butanol mixture, the variation with the temperature is shown in Figure 4.8. Similarly, Figure 4.9 shows for the 1,2-epoxybutane + three alkanols systems Finally, the mixtures containing ethyl formate with benzene and cyclohexane are shown in Figure 4.10.

In Figures 4.1 - 4.6 and Figure 4.8, it can be observed that as the temperature increases the equilibrium pressure of system and vapor pressure of pure components increase at constant composition. These results provide support for the fact that the vapor pressure is dependent on temperature.

In Figure 4.9, the regular increase of the pressures in passing from 2-propanol to methanol. In addition, in Figure 4.10, the pressure values of the ethyl formate (1) with cyclohexane (2) system are higher than of the ethyl formate (1) with benzene (2) system.

As observed in Figures 4.1, 4.3, and Figures 4.8 - 4.10, the partial pressures for these binary mixtures were higher than those calculated from Raoult's law (positive deviation).

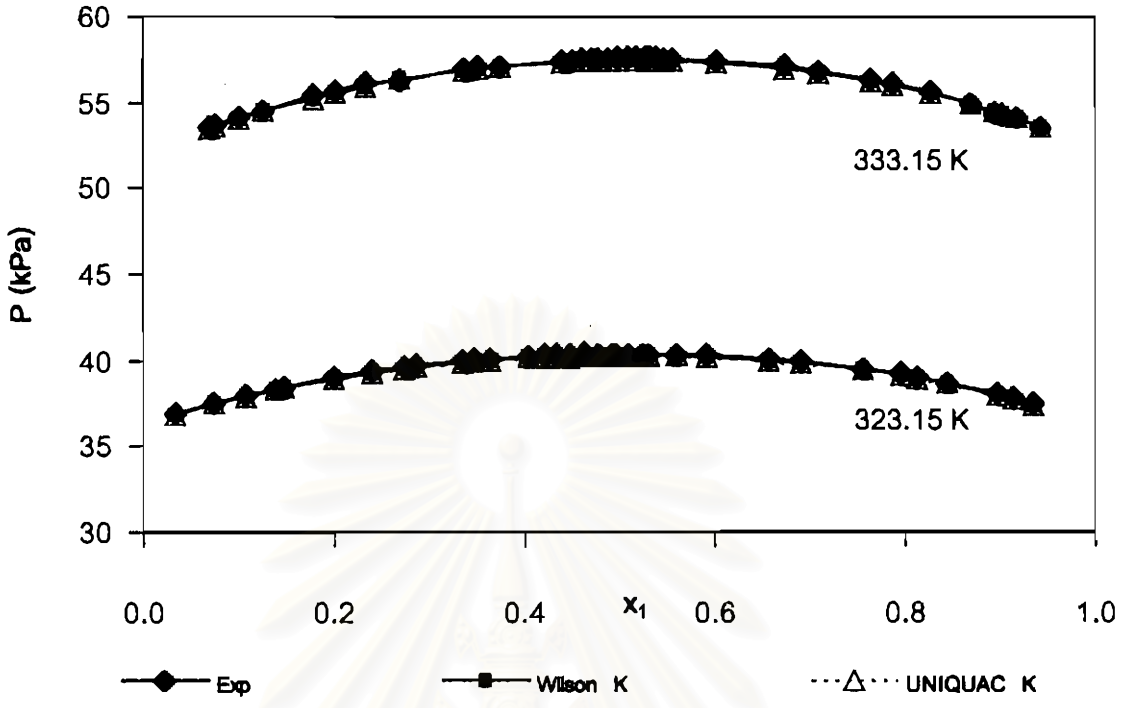

Figure 4.1 P (kPa) of benzene (1) and cyclohexane (2) system at 323.15 and 333.15 K (Kurihara et al., 1997).

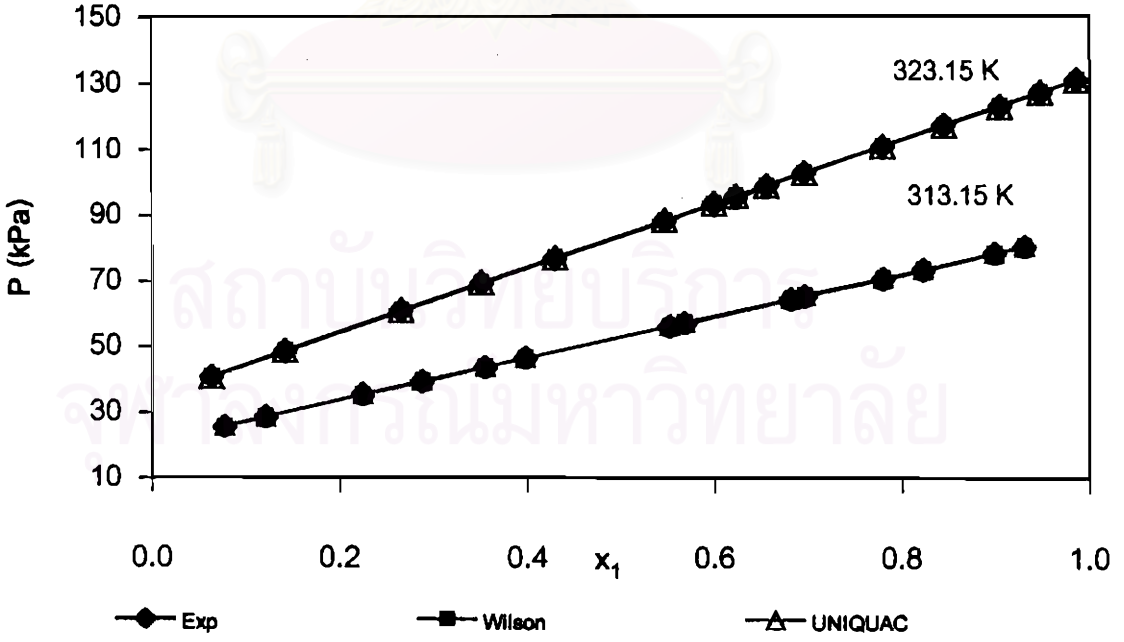

Figure 4.2 P (kPa) of 1-chloropentane (1) and di-n-butyl ether (2) system at 313.15 and 323.15 K (Paul et al., 1986).

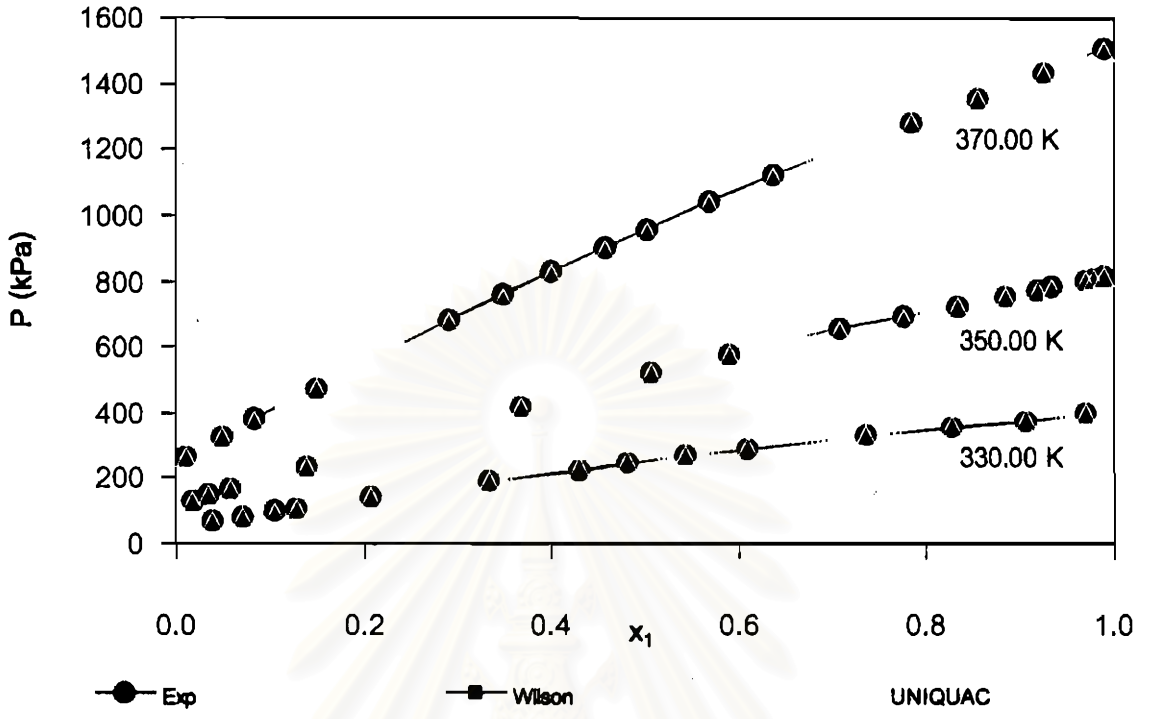

Figure 4.3 P (kPa) of 1,2-dichloroethane (1) and di-n-butyl ether (2) system at 330.00, 350.00 and 370.00 K (Paul et al., 1986).

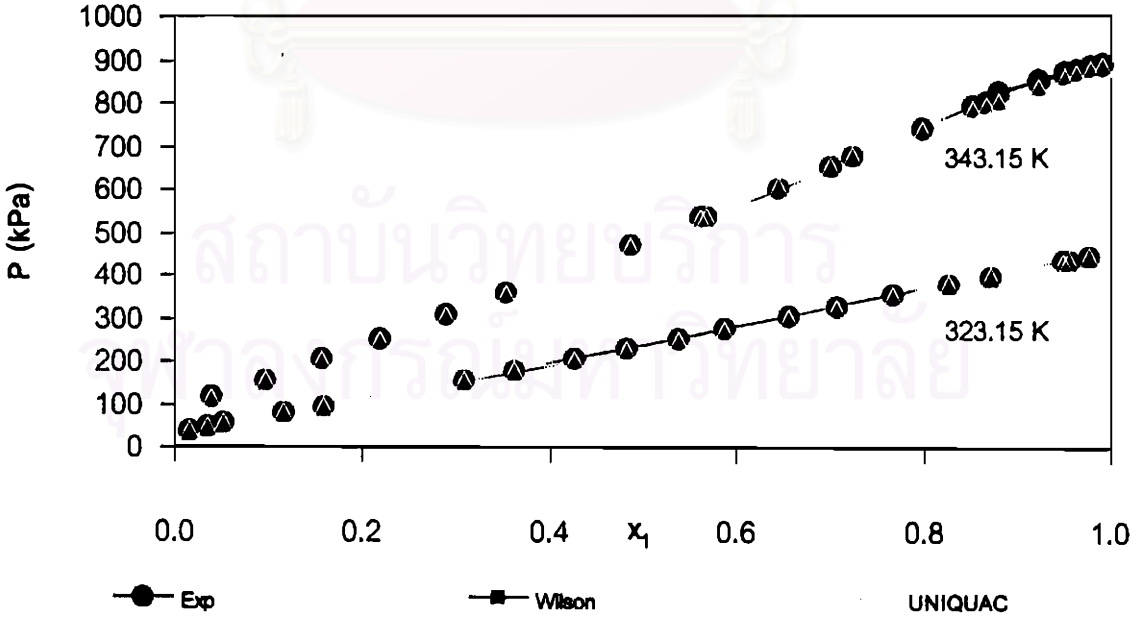

Figure 4.4 P (kPa) of 1,1,1-trichloroethane (1) and di-n-butyl ether (2) system at 323.15 and 343.15 K (Paul et al., 1986).

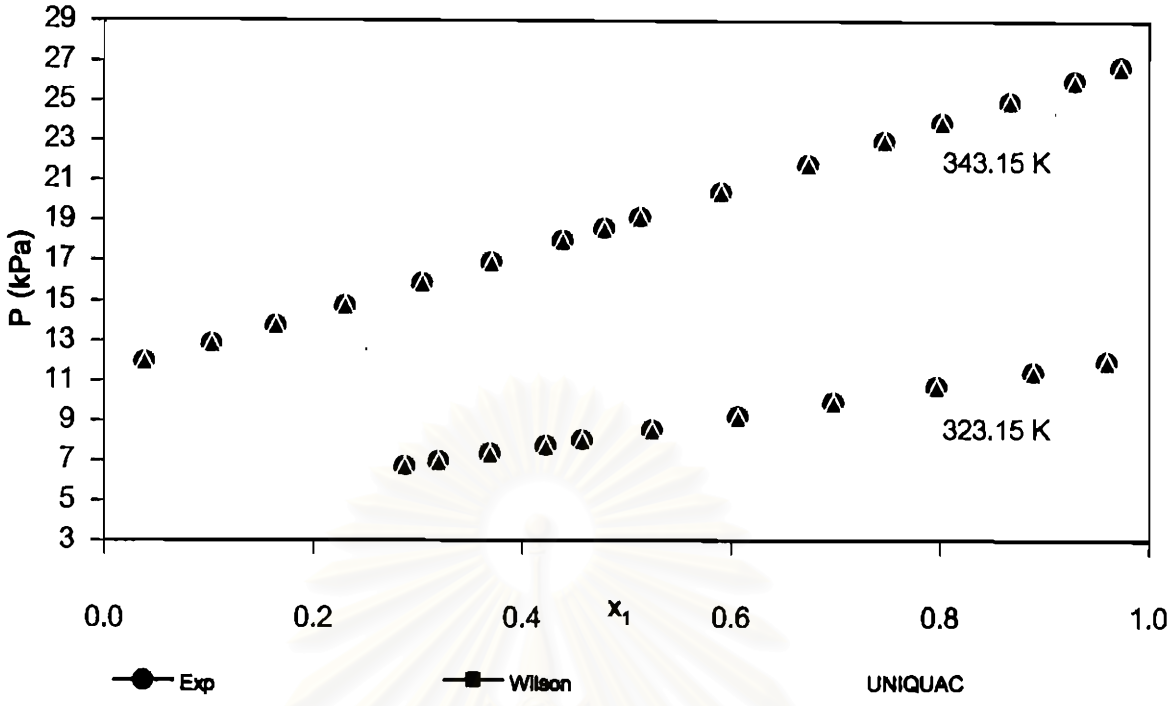

Figure 4.5 P (kPa) of toluene (1) and 1-chlorohexane (2) system at 323.15 and 343.15 K (Paul et al., 1988).

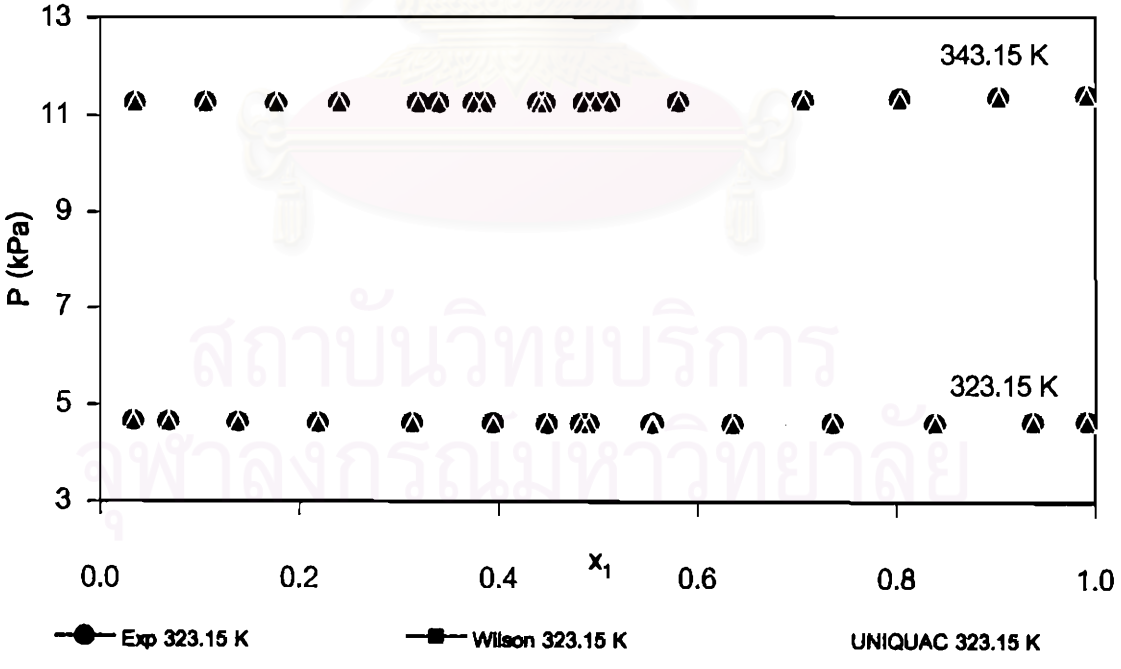

Figure 4.6 P (kPa) of 1-chlorohexane (1) and ethylbenzene (2) system at 323.15 and 343.15 K (Paul et al., 1988).

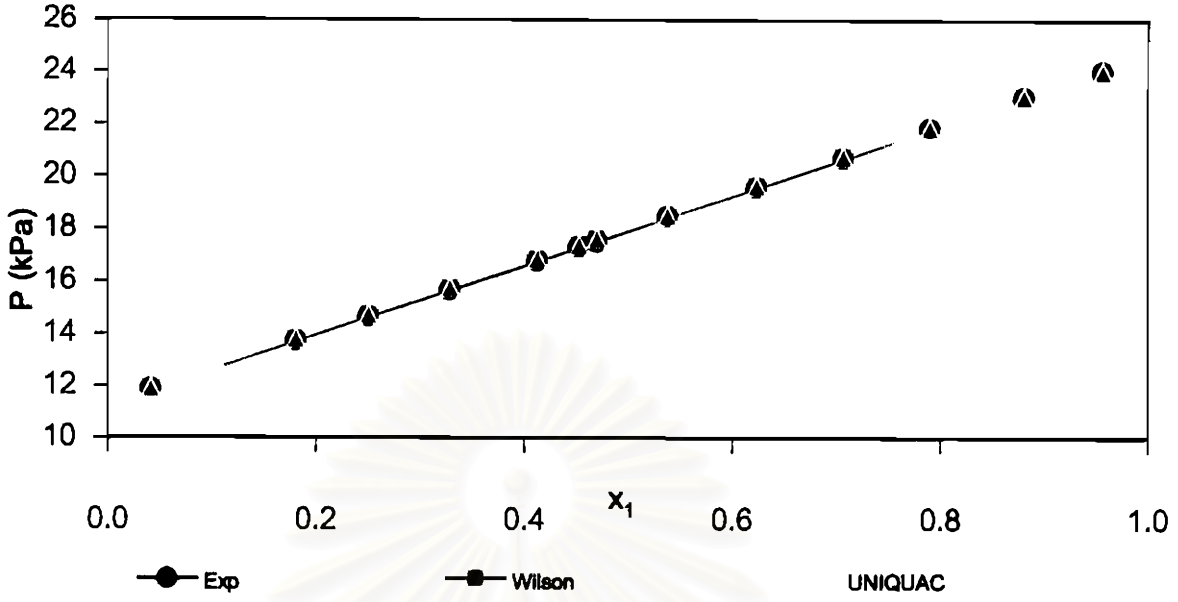

Figure 4.7 P (kPa) of 1-chlorohexane (1) and n-propylbenzene (2) system at 363.15 K (Paul et al., 1988).

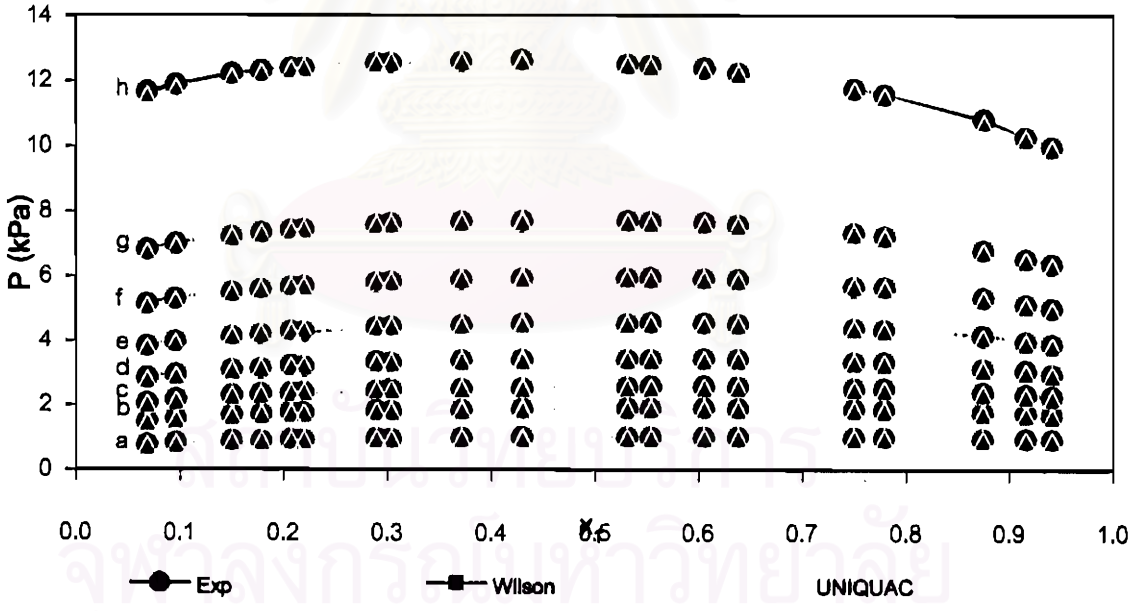

Figure 4.8 P (kPa) of butanenitrile (1) and 2-butanol (2) at (a) 278.15, (b) 288.15, (c) 293.15, (d) 298.15, (e) 303.15, (f) 308.15, (g) 313.15, and (h) 323.15 K (Garriga et al., 1997).

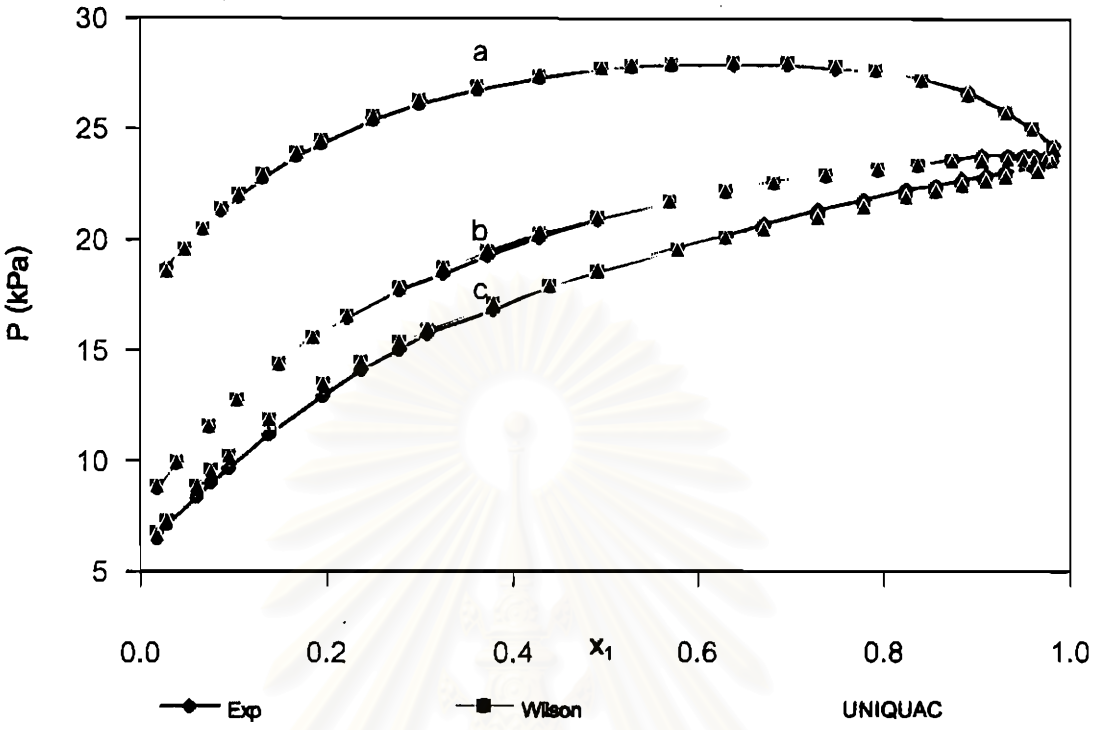

Figure 4.9 P (kPa) for the binary mixtures containing 1,2-epoxybutane (1) + (a) methanol (2), + (b) ethanol (2), and + (c) 2-propanol (2) at 298.15 K (Comelli et al., 1996).

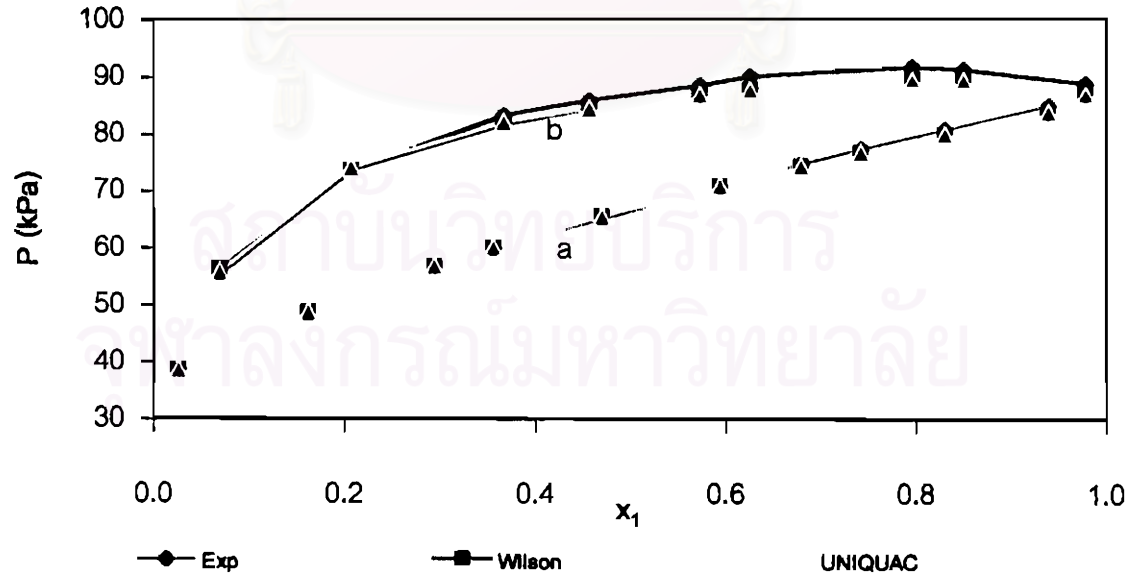

Figure 4.10 P (kPa) for the binary mixtures containing ethyl formate (1) + (a) benzene (2), + (b) cyclohexane (2) at 323.15 K (Ohta et al., 1980).

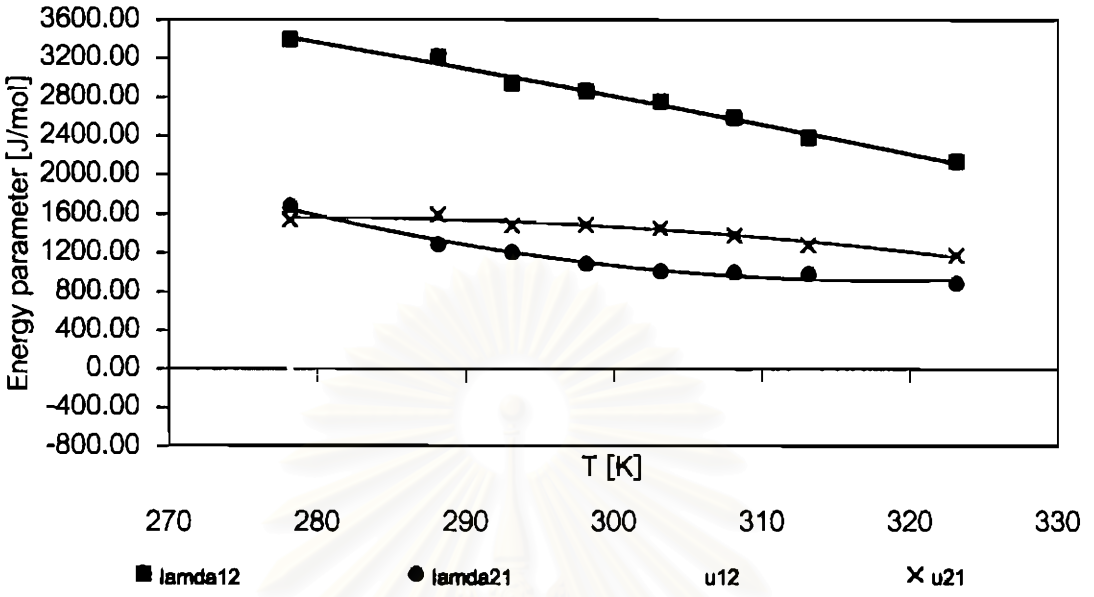

Figure 4.11 Wilson and UNIQUAC parameters of butanenitrile (1) and 2-butanol (2) system (Garriga et al., 1997).

Table 4.3 Binary constants of Wilson and UNIQUAC equations for butanenitrile (1) and 2-butanol (2) system.

binary constants					
Wilson			UNIQUAC		
A_1	B_1	C_1	A_1	B_1	C_1
A_2	B_2	C_2	A_2	B_2	C_2
[J mol^{-1}]	[J mol^{-1} K^{-1}]	[J mol^{-1}K^{-2}]	[J mol^{-1}]	[J mol^{-1} K^{-1}]	[J mol^{-1} K^{-2}]
6818.9	1.95	-0.0511	19871	-131.23	0.2144
46187.0	-284.16	0.4459	-14306	113.77	-0.2040

The percent average absolute deviations between the values calculated by the Wilson and UNIQUAC equations and the literature values are less than about 2.26% in all cases. It indicates that all equations give a good fit of the data.

The butanenitrile + 2-butanol system in Table 4.2 and Figure 4.11 show the binary parameters of all equations are dependent on temperature. They were expressed in a quadratic function of temperature by means of

$$A_{ij} = A_i + B_iT + C_iT^2 \qquad (4.1)$$

where A_{ij} is the interaction energy parameter. The constant A, B, C are given in Table 4.3.

4.2 Excess Enthalpies

The excess enthalpies were correlated by the Wilson and UNIQUAC equations and the parameters for all the mixtures are set out in Table 4.4 along with the percentage average absolute deviations between the calculated and experimental excess enthalpies %AAD (H^E). In this case the values of the parameters were obtained by iteration, minimizing the objective function (Eq. 3.1) to achieve the best fit. Figures 4.12 - 4.24 plots the experimental points and the fitted curves using the Wilson and UNIQUAC equations for comparison.

At the studied temperatures there are no change in sign of the excess enthalpy of thirteen binary mixtures.

Figures 4.12 - 4.20, all binary mixtures show positive H^E values (heat is absorbed) since energy intake for breaking intermolecular forces between molecules belonging to the same component prevails over the energy released by interacting dissimilar molecules. On the contrary, in Figures 4.21 - 4.24, the H^E values are negative (heat is evolved).

Table 4.4 Parameters and percent average absolute deviations ,%AAD (H^E) of Wilson and UNIQUAC equations using H^E data.

	Wilson			UNIQUAC		
T /K	λ_{12} J/mol	λ_{21} J/mol	%AAD (H^E)	u_{12} J/mol	u_{21} J/mol	%AAD (H^E)
Benzene (1) + Cyclohexane (2)						
298.15[a]	3544.46	3912.77	10.65	426.24	926.90	0.25
298.15[b]	3456.60	3845.40	10.43	431.31	916.62	0.44
298.15[c]	3905.18	4235.35	11.64	435.68	884.84	0.35
298.15[d]	3297.13	3555.72	9.28	433.48	924.27	0.48
1-Chloropentane (1) + Di-n-butyl ether (2)						
288.15	354.37	-348.79	14.59	-353.58	434.40	1.30
298.15	1285.16	-1021.18	9.34	-410.36	524.09	1.27
313.15	1767.52	-1227.25	24.19	-438.66	579.14	2.89
1,2-Dichloroethane (1) + Di-n-butyl ether(2)						
288.15	964.26	2151.30	0.89	446.25	150.54	1.47
298.15	1059.81	2621.60	0.62	541.14	120.09	0.95
1,1,1-Trichloroethane (1) + Di-n-butyl ether(2)						
283.15	316.24	-850.67	2.82	-811.89	133.39	4.66
298.15	347.49	-845.68	1.38	1052.55	-793.64	4.04
308.15	474.62	-924.21	0.93	1039.55	-782.93	2.42
Toluene (1) + 1-Chlorohexane (2)						
288.15	-93.71	-746.51	1.73	-575.08	443.03	1.59
298.15	-112.63	-676.48	1.41	-524.16	383.75	1.27
1-Chlorohexane (1) + Ethylbenzene (2)						
288.15	-383.65	-248.72	1.36	60.98	-222.20	1.27
298.15	-408.05	-190.35	0.59	132.07	-274.71	0.54
1-Chlorohexane (1) + n-Propylbenzene (2)						
288.15	-232.88	-430.68	0.71	-106.16	-62.19	0.64
298.15	-245.82	-377.22	2.03	-57.17	-99.54	1.97

Table 4.4 (continued)

T /K	Wilson λ_{12} J/mol	Wilson λ_{21} J/mol	Wilson %AAD (P)	UNIQUAC u_{12} J/mol	UNIQUAC u_{21} J/mol	UNIQUAC %AAD (P)
			1,2-Epoxybutane (1) + Methanol (2)			
298.15	1140.30	3827.50	14.61	2582.94	257.04	11.51
			1,2-Epoxybutane (1) + Ethanol (2)			
298.15	3941.93	7923.55	41.60	3133.61	645.35	9.58
			1,2-Epoxybutane (1) + 2-Propanol (2)			
298.15	5289.61	8173.20	55.32	2667.23	1429.07	11.66
			Ethyl formate (1) + Benzene (2)			
298.15	1983.99	413.01	4.23	-43.86	875.60	5.24
308.15	1359.12	501.65	2.17	150.59	508.25	2.48
318.15	1234.06	459.32	1.92	162.41	446.92	2.32
			Ethyl formate (1) + Cyclohexane (2)			
298.15	6490.56	5806.71	61.16	1054.44	2448.49	1.20
308.15	7529.74	6305.20	61.11	1022.63	2427.15	1.33
			Butanenitrile (1) + 2-Butanol (2)			
298.15	6897.26	5811.82	70.45	2179.20	2843.77	2.86

[a] Stokes et al., 1969.

[b] Kuus et al., 1996.

[c] Meyer et al., 1977.

[d] Hsu et al., 1975.

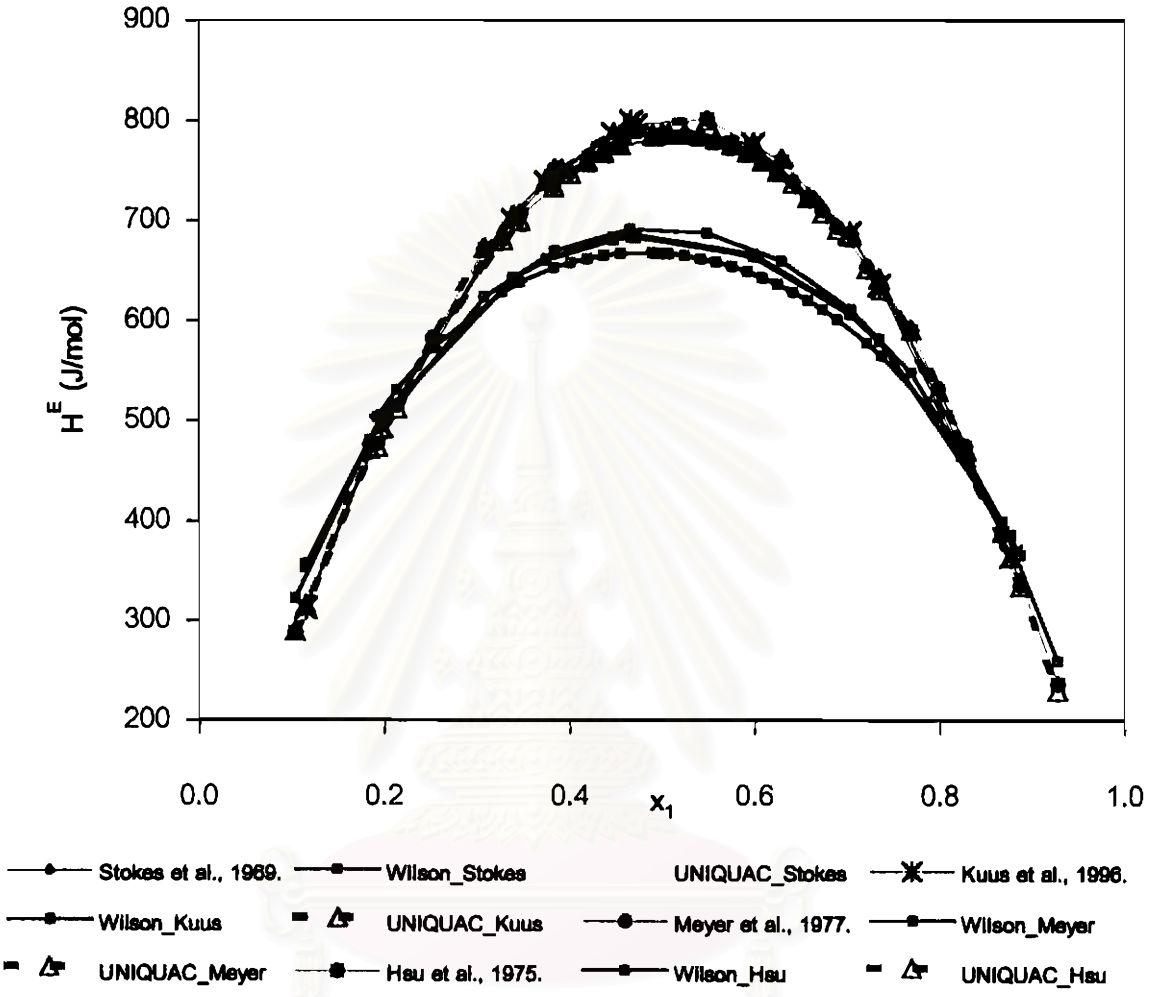

Figure 4.12 H^E (J/mol) of benzene (1) and cyclohexane (2) system at 298.15 K (Stokes et al., 1969; Hsu et al., 1975; Meyer et al., 1977; and Kuus et al., 1996).

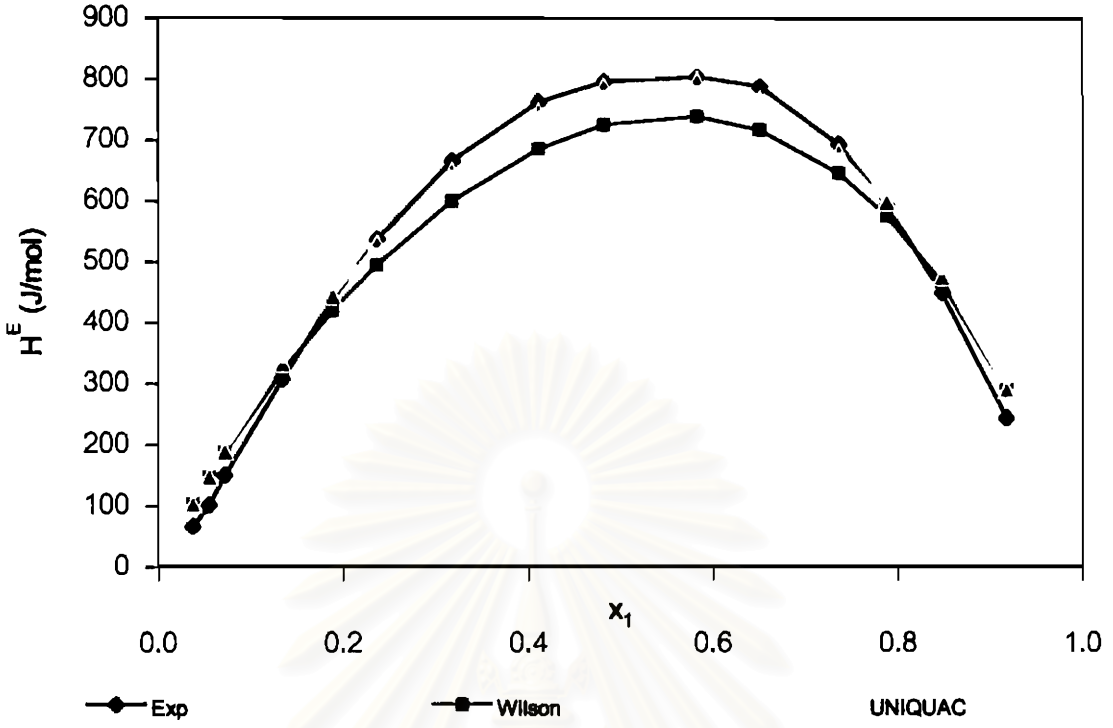

Figure 4.13 H^E (J/mol) of 1,2-epoxybutane (1) and methanol (2) system at 298.15 K (Comelli et al., 1996).

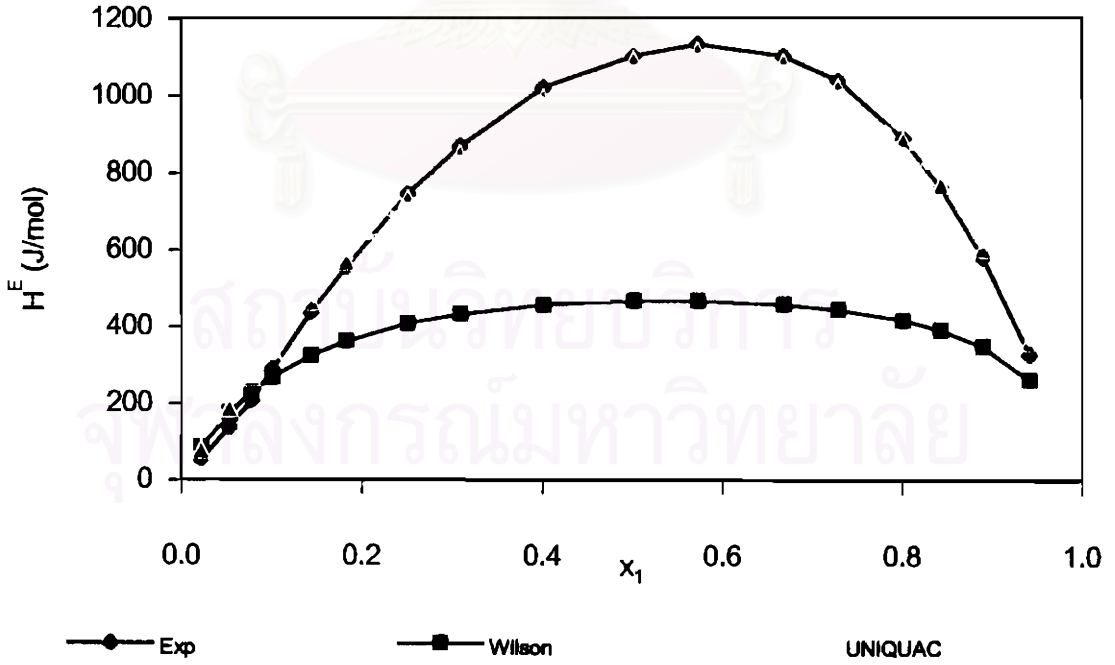

Figure 4.14 H^E (J/mol) of 1,2-epoxybutane (1) and ethanol (2) system at 298.15 K (Comelli et al., 1996).

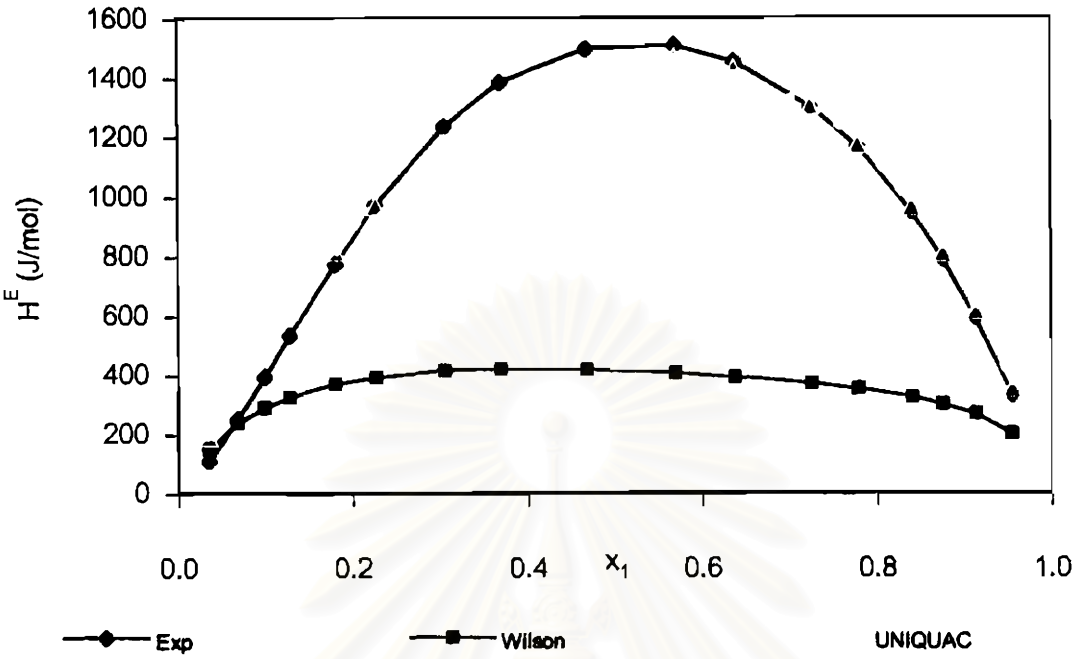

Figure 4.15 H^E (J/mol) of 1,2-epoxybutane (1) and 2-propanol (2) system at 298.15 K (Comelli et al., 1996).

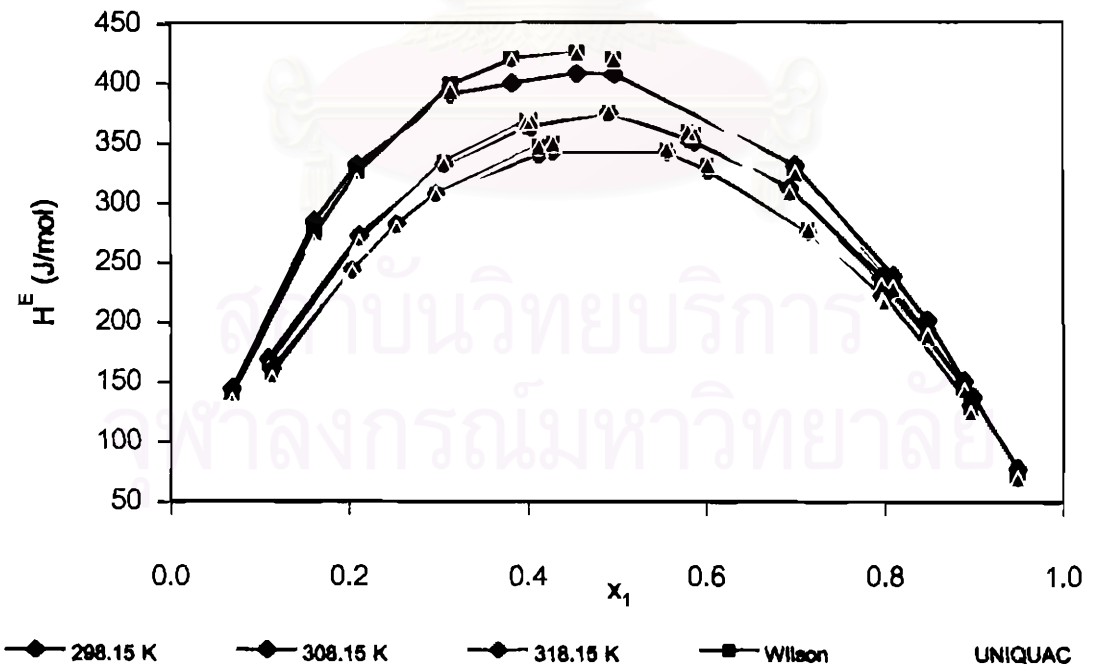

Figure 4.16 H^E (J/mol) of ethyl formate (1) and benzene (2) system at 298.15, 308.15, and 318.15 K (Ohta et al., 1980).

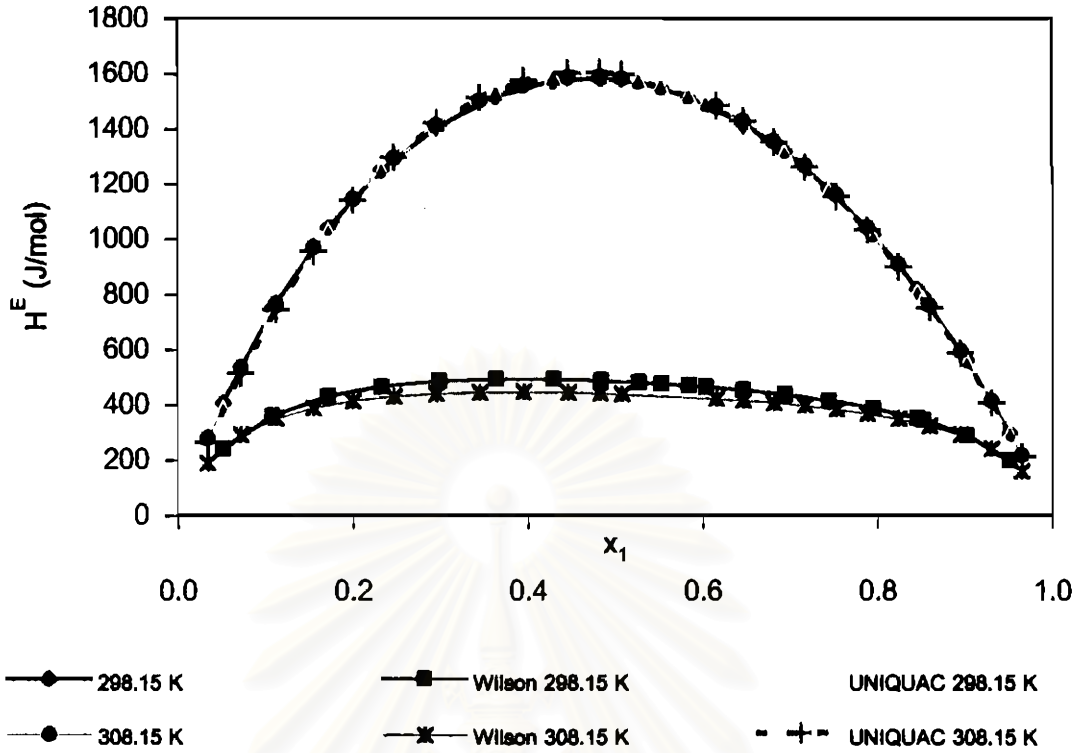

Figure 4.17 H^E (J/mol) of ethyl formate (1) and cyclohexane (2) system at 298.15 and 308.15 K (Ohta et al., 1980).

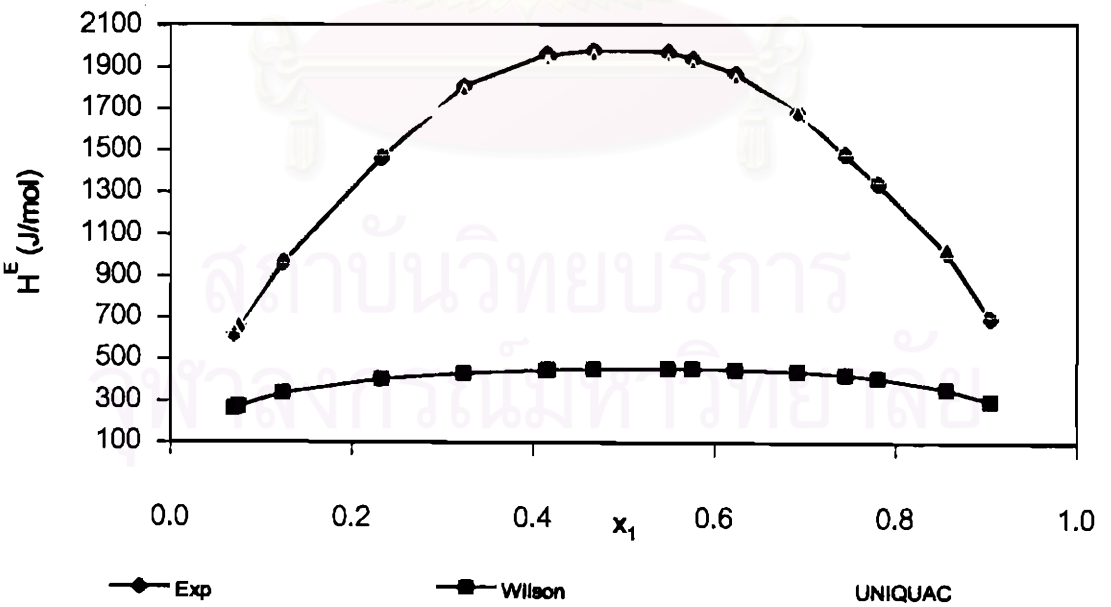

Figure 4.18 H^E (J/mol) of butanenitrile (1) and 2-butanol (2) system at 298.15 K (Garriga et al., 1997).

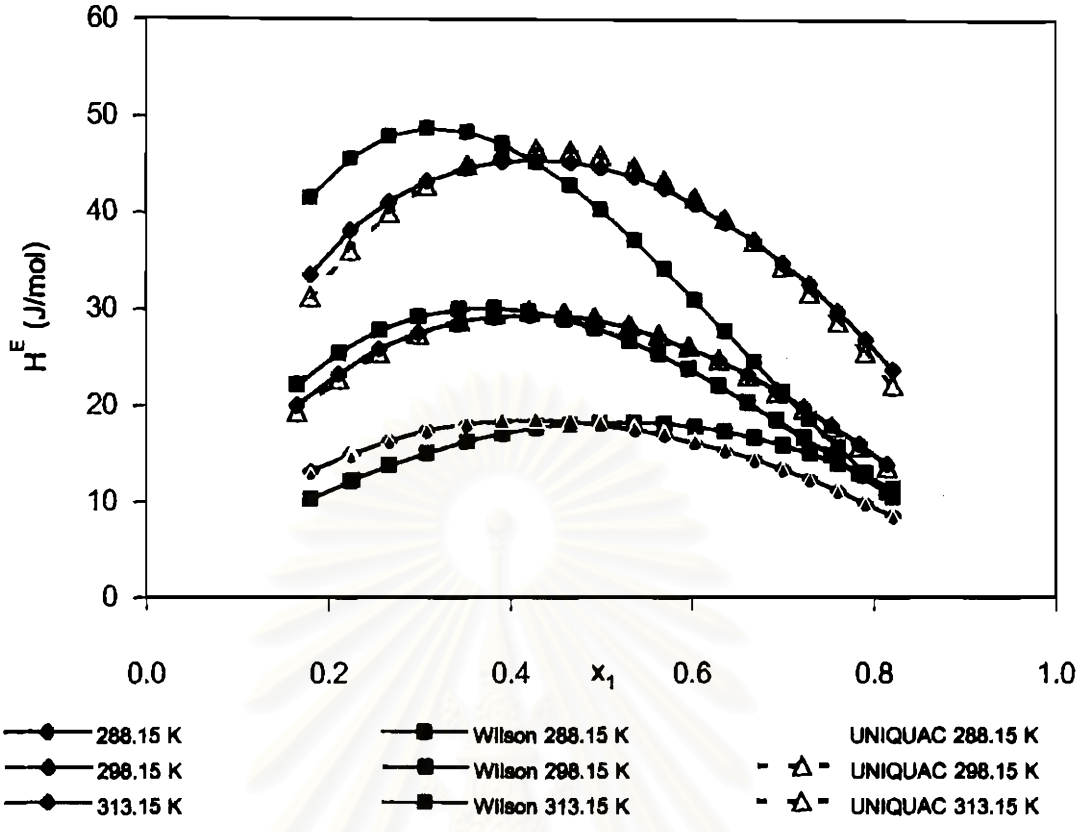

Figure 4.19 H^E (J/mol) of 1-chloropentane (1) and di-n-butyl ether (2) system at 288.15, 298.15 and 313.15 K (Paul et al., 1986).

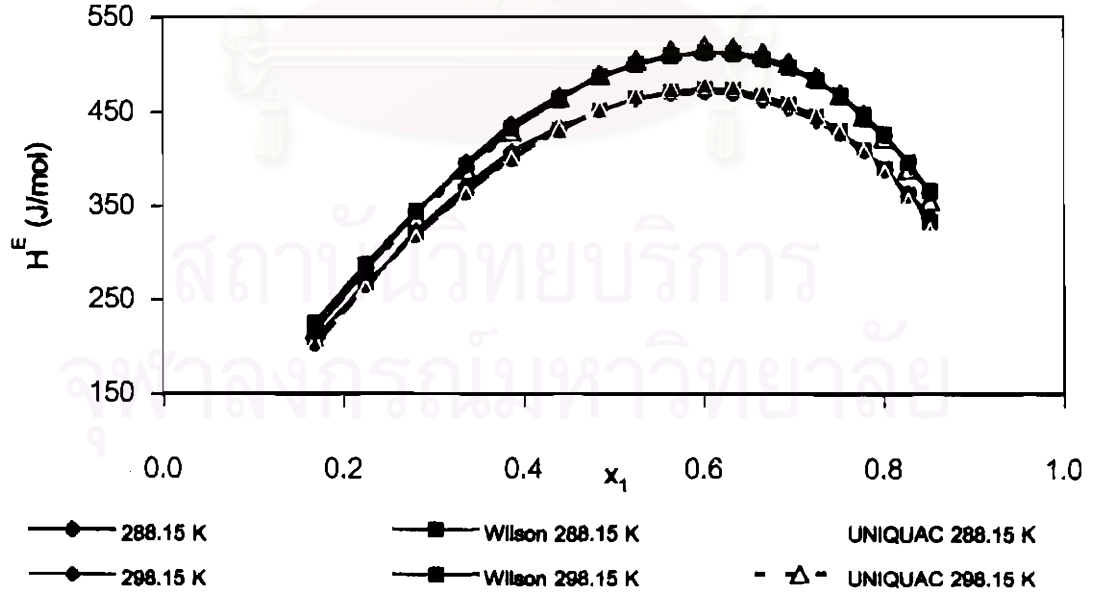

Figure 4.20 H^E (J/mol) of 1,2-dichloroethane (1) and di-n-butyl ether (2) system at 288.15 and 298.15 K (Paul et al., 1986).

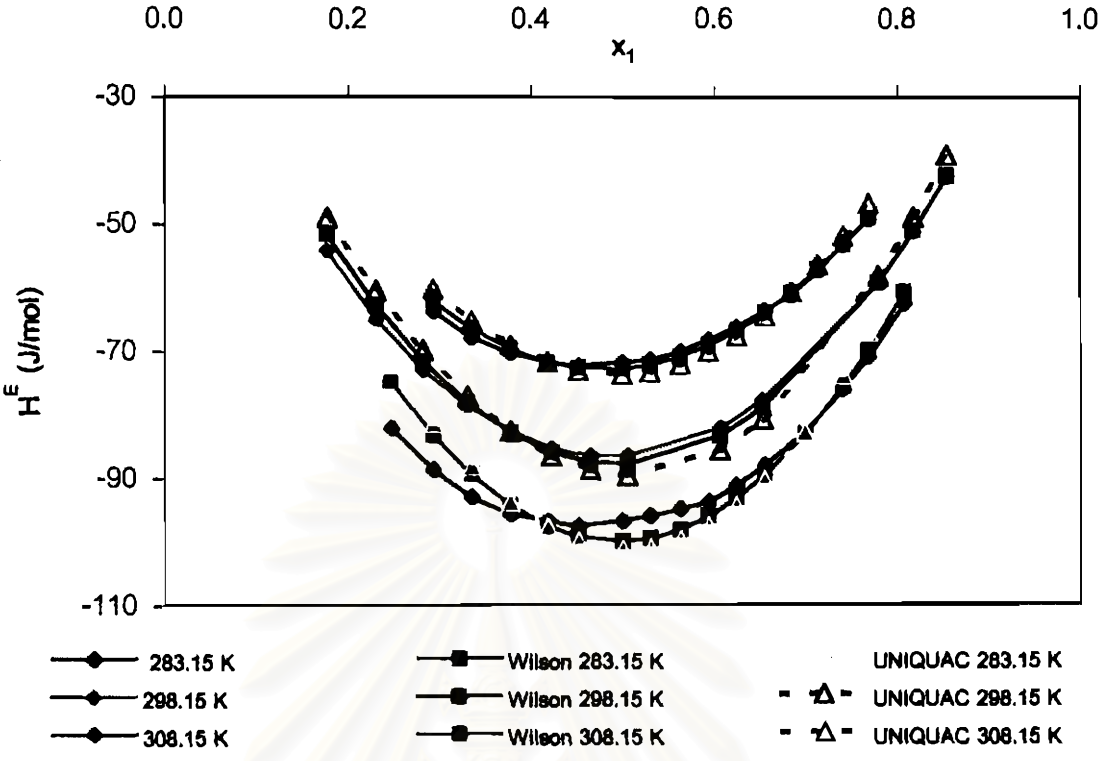

Figure 4.21 H^E (J/mol) of 1,1,1-trichloroethane (1) and di-n-butyl ether (2) system at 283.15, 298.15, and 308.15 K (Paul et al., 1986).

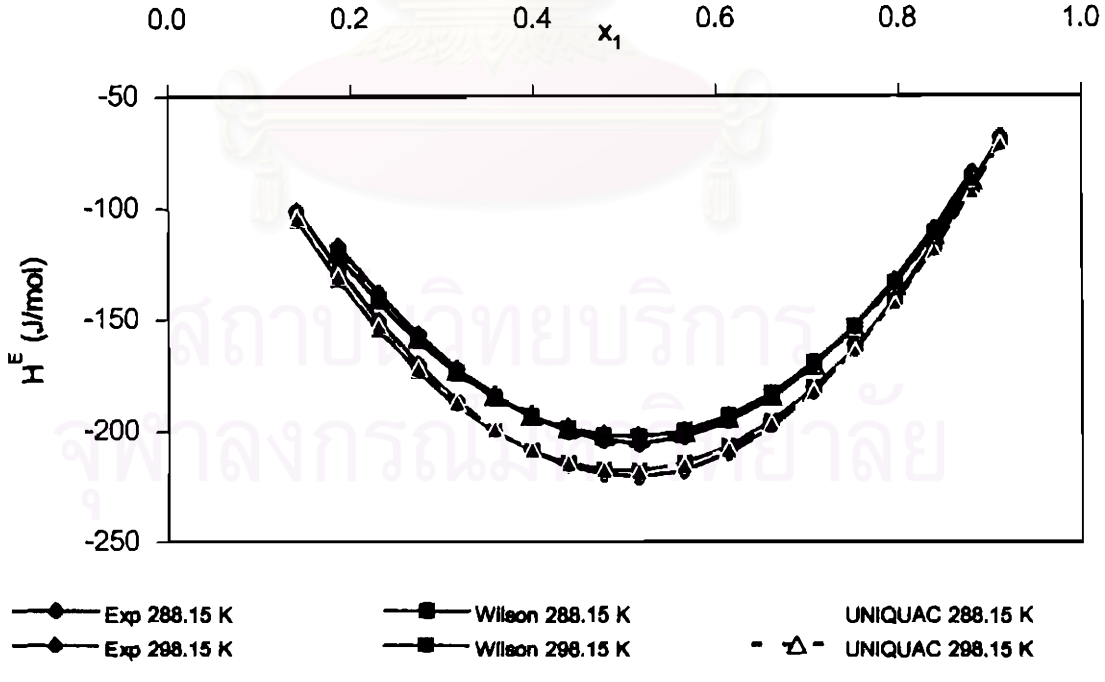

Figure 4.22 H^E (J/mol) of toluene (1) and 1-chlorohexane (2) system at 288.15 and 298.15 K (Paul et al., 1988).

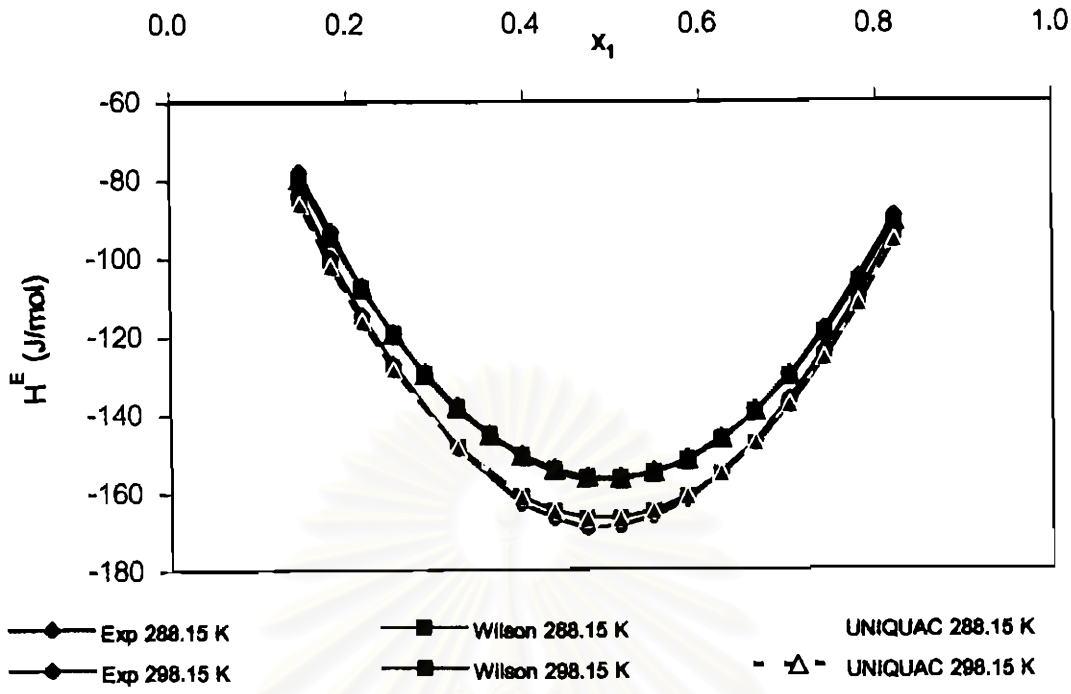

Figure 4.23 H^E (J/mol) of 1-chlorohexane (1) and ethylbenzene (2) system at 288.15 and 298.15 K (Paul et al., 1988).

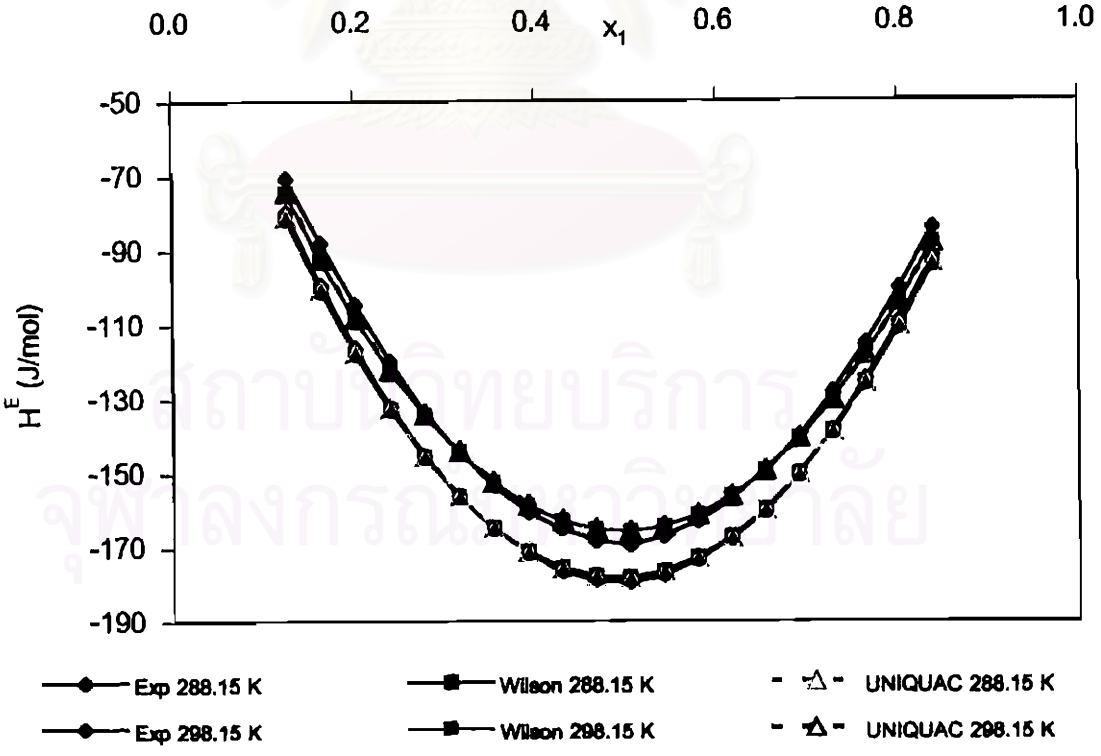

Figure 4.24 H^E (J/mol) of 1-chlorohexane (1) and *n*-propylbenzene (2) system at 288.15 and 298.15 K (Paul et al., 1988).

The percent average absolute deviations obtained by the Wilson equation as shown in Table 4.4 lie in the neighborhood of 41.60 - 70.75% for the 1,2-epoxybutane + ethanol, 1,2-epoxybutane + 2-propanol, ethyl formate + cyclohexane, and butanenitrile + 2-butanol systems but are in the region 0.59 - 14.61% for the other systems. Moreover, the deviations are less than about 11.7% in all cases by using the UNIQUAC model. It indicates that prediction by UNIQUAC model is better than the other equation.

The predictions using the Wilson and UNIQUAC equations give a good fit of the data for the 1,2-dichloroethane (1) with di-n-butyl ether (2), 1,1,1-trichloroethane (1) with di-n-butyl ether (2), toluene (1) with 1-chlorohexane (2), 1-chlorohexane (1) with ethylbenzene (2) and 1-chlorohexane (1) with n-propylbenzene (2) systems since the %AAD values are less than about 5%.

4.3 Calculated excess enthalpy based on parameters from VLE data

The H^E-calculated values using the fitted Wilson and UNIQUAC parameters in Table 4.2 are shown as curve in Figures 4.25 through 4.44 together with the H^E experimental data, at the same temperature. The percent average absolute deviations of the excess enthalpies, %AAD (H^E) are presented in Table 4.5.

The percent average absolute deviations between the values calculated by the Wilson and UNIQUAC equations and the literature values are more than about 11% in all cases. It indicates that all equations give a poor fit of the data.

As observed, the predicted results by the Wilson equation are superior to the UNIQUAC equation except for the butanenitrile + 2-butanol systems. Unfortunately, results for thirteen binary systems leads to a worsening of the fit excess enthalpy values from VLE data.

Table 4.5 %AAD in H^E for thirteen binary systems based on parameters from VLE data.

Systems	No of Data	T/K	%AAD (H^E)	
			Wilson	UNIQUAC
benzene + cyclohexane	11[a]	298.15	70.53	69.67
	11[b]	298.15	70.67	69.81
	11[c]	298.15	71.57	70.43
	29[d]	298.15	68.15	69.68
1,2-epoxybutane + methanol	15[e]	298.15	28.27	30.80
1,2-epoxybutane + ethanol	17[e]	298.15	56.74	58.52
1,2-epoxybutane + 2-propanol	17[e]	298.15	63.60	60.66
ethyl formate + benzene	12[f]	298.15	44.12	83.71
	11[f]	308.15	36.74	80.88
	12[f]	318.15	30.42	79.21
ethyl formate + cyclohexane	20[f]	298.15	58.84	63.07
	23[f]	308.15	54.92	61.93
1-chlorohexane + n-propylbenzene	20[g]	288.15	39.64	225.42
	20[g]	298.15	41.21	235.51
toluene + 1-chlorohexane	19[f]	288.15	23.89	212.88
	17[f]	298.15	22.90	217.23
	19[h]	288.15	37.16	237.97
	17[h]	298.15	35.60	242.94
1-chlorohexane + ethylbenzene	17[f]	288.15	82.36	36.20
	19[f]	298.15	79.01	32.68
	17[h]	288.15	30.93	240.54
	19[h]	298.15	36.27	247.93
1-chloropentane + di-n-butyl ether	20[i]	288.15	315.44	445.24
	19[i]	298.15	228.09	291.60
	19[i]	313.15	153.15	196.39
	20[f]	288.15	151.41	219.80
	19[f]	298.15	98.47	157.72
	19[f]	313.15	70.52	120.12

Table 4.5 (continued)

Systems	No of data	T/K	%AAD(H^E)	
			Wilson	UNIQUAC
1,2-dichloroethane + di-n-butyl ether	19[j]	288.15	18.69	24.36
	19[j]	298.15	24.23	29.54
	19[k]	288.15	11.01	16.34
	19[k]	298.15	14.76	22.62
	19[l]	288.15	21.61	23.01
	19[l]	298.15	27.20	28.77
1,1,1-trichloroethane + di-n-butyl ether	13[f]	283.15	1031.75	399.39
	16[f]	298.15	1157.54	408.16
	15[f]	308.15	1295.25	496.08
	13[h]	283.15	195.36	695.13
	16[h]	298.15	127.96	716.46
	15[h]	308.15	231.45	869.75
butanenitrile + 2-butanol	16[m]	298.15	66.81	61.66
	16[n]	298.15	66.19	69.22
	16[o]	298.15	70.11	67.56
	16[e]	298.15	71.10	69.25
	16[p]	298.15	71.84	70.32
	16[q]	298.15	72.32	70.87
	16[l]	298.15	73.05	71.62
	16[f]	298.15	74.64	73.59

[a] Kuus, 1996. [b] Stokes, 1969. [c] Hsu, 1975. [d] Meyer, 1977.

[e] parameters from VLE data at 298.15 K [f] parameters from VLE data at 323.15 K

[g] parameters from VLE data at 363.15 K [h] parameters from VLE data at 343.15 K

[i] parameters from VLE data at 313.15 K [j] parameters from VLE data at 330.00 K

[k] parameters from VLE data at 350.00 K [l] parameters from VLE data at 370.00 K

[m] parameters from VLE data at 278.15 K [n] parameters from VLE data at 288.15 K

[o] parameters from VLE data at 293.15 K [p] parameters from VLE data at 303.15 K

[q] parameters from VLE data at 308.15 K

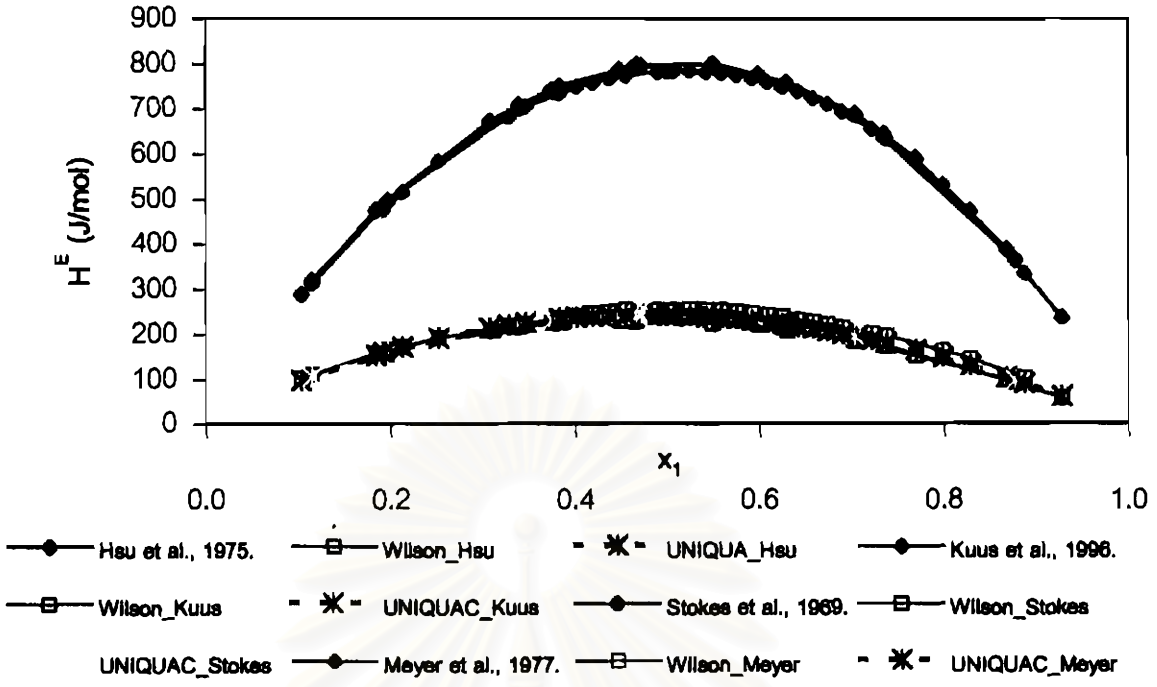

Figure 4.25 H^E (J/mol) of benzene (1) and cyclohexane (2) system at 298.15 K based on parameters from VLE data at 323.15 K.

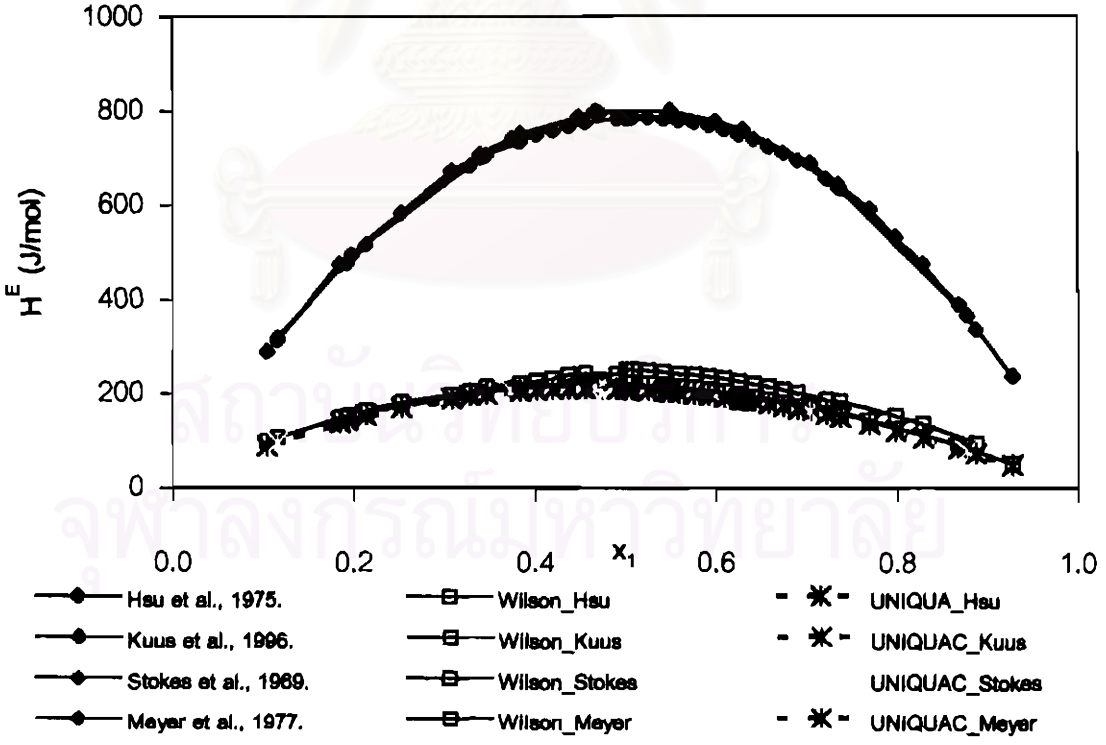

Figure 4.26 H^E (J/mol) of benzene (1) and cyclohexane (2) system at 298.15 K based on parameters from VLE data at 333.15 K.

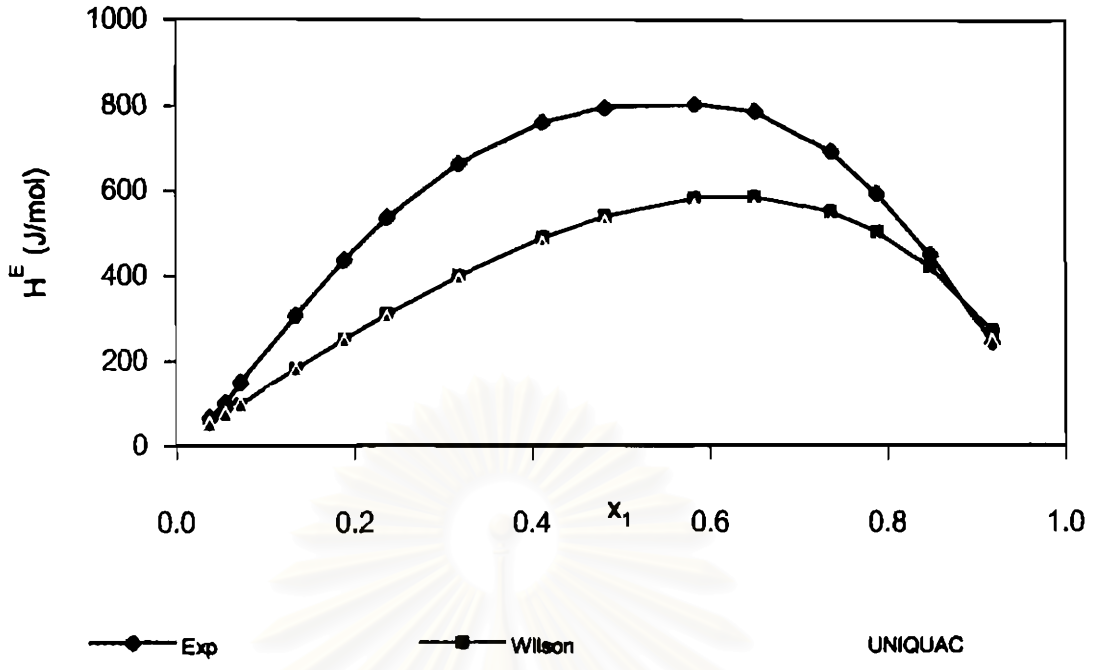

Figure 4.27 H^E (J/mol) of 1,2-epoxybutane (1) and methanol (2) system at 298.15 K based on parameters from VLE data at 298.15 K.

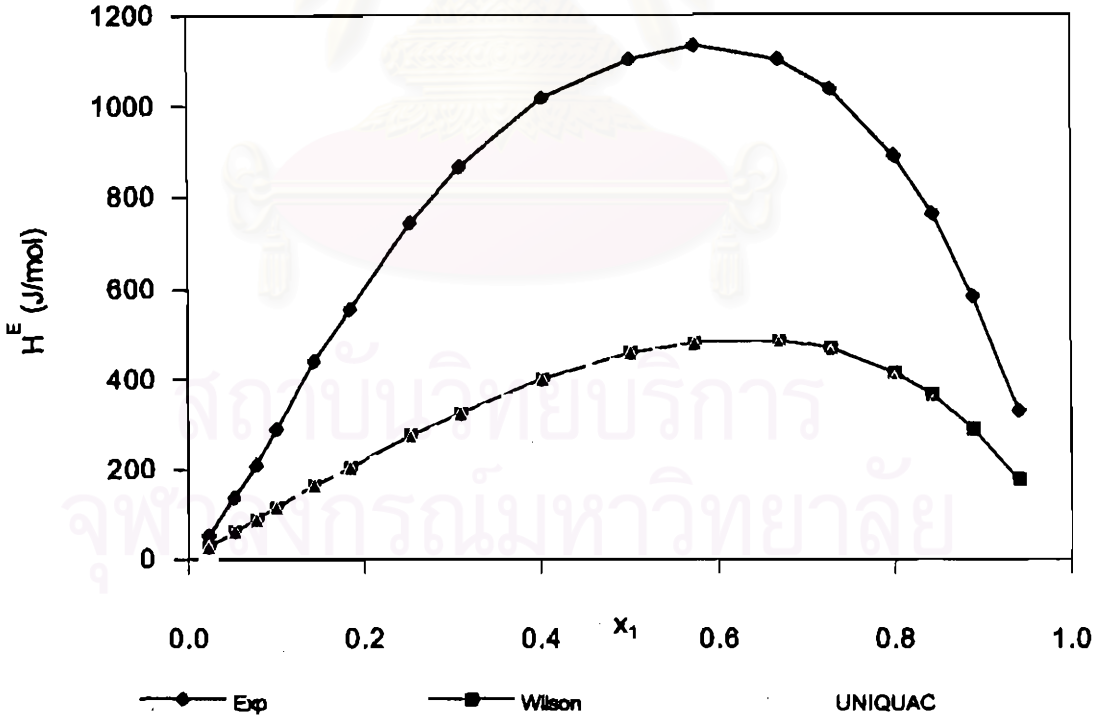

Figure 4.28 H^E (J/mol) of 1,2-epoxybutane (1) and ethanol (2) system at 298.15 K based on parameters from VLE data at 298.15 K.

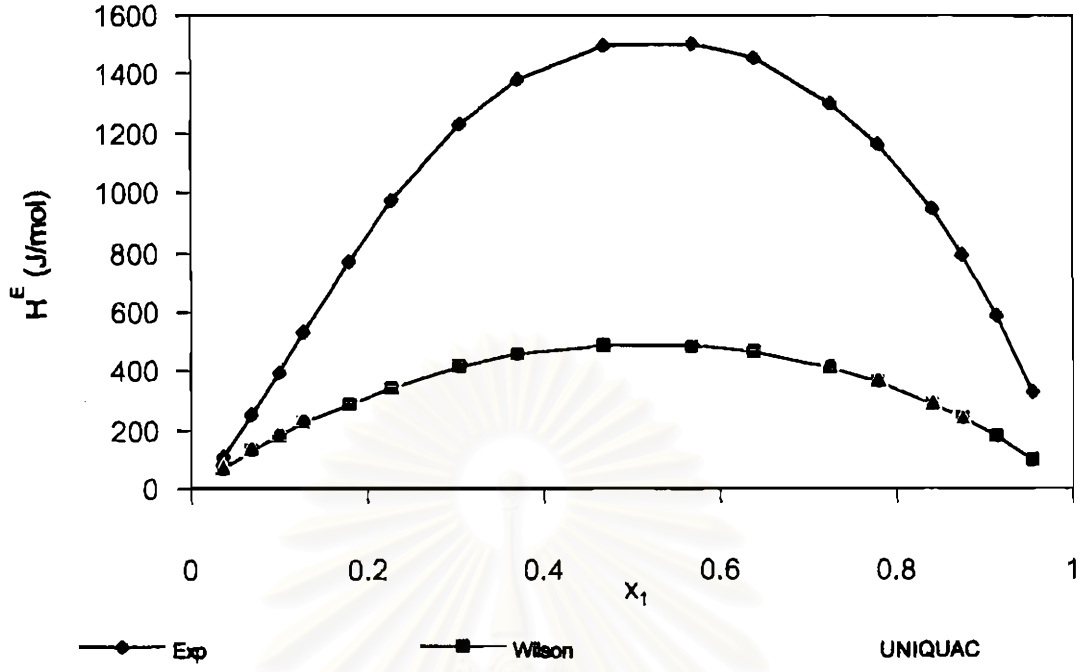

Figure 4.29 H^E (J/mol) of 1,2-epoxybutane (1) and 2-propanol (2) system at 298.15 K based on parameters from VLE data at 298.15 K.

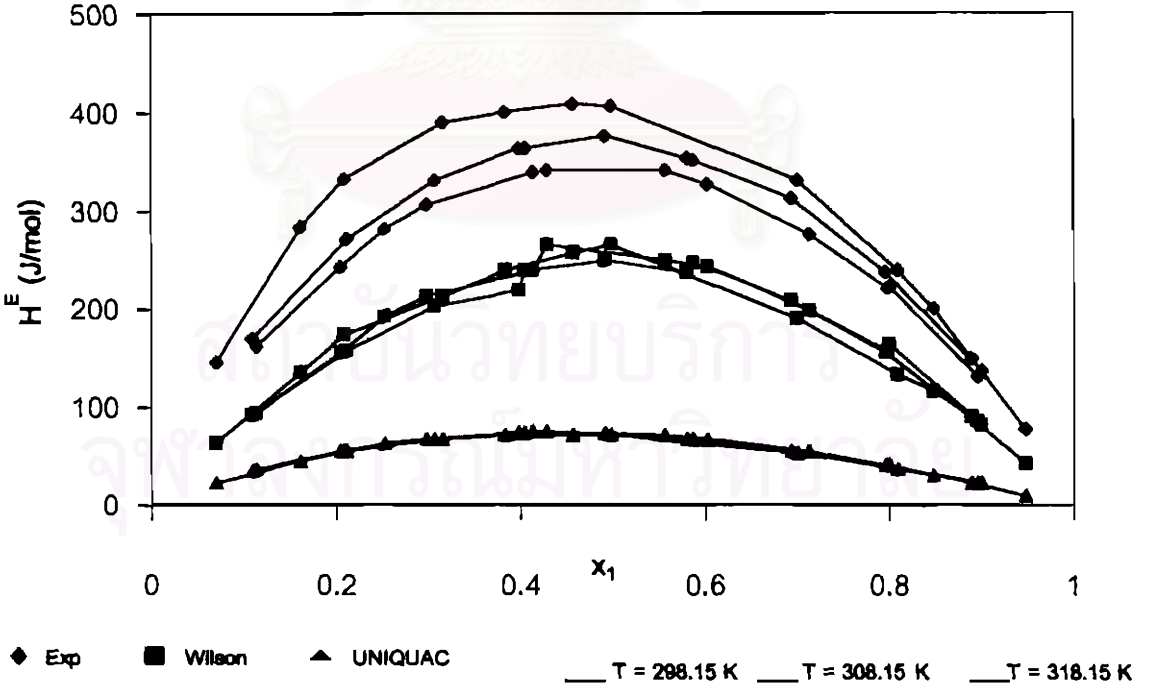

Figure 4.30 H^E (J/mol) of ethyl formate (1) and benzene (2) system based on parameters from VLE data at 323.15 K.

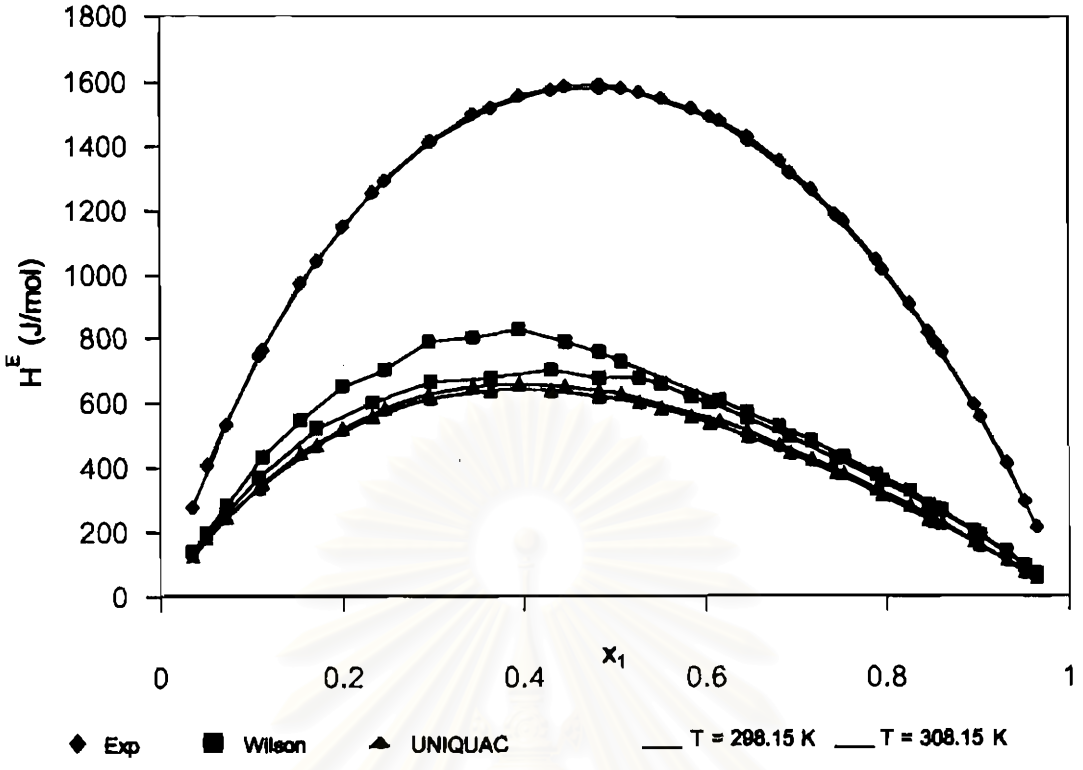

Figure 4.31 H^E (J/mol) of ethyl formate (1) and cyclohexane (2) system based on parameters from VLE data at 323.15 K.

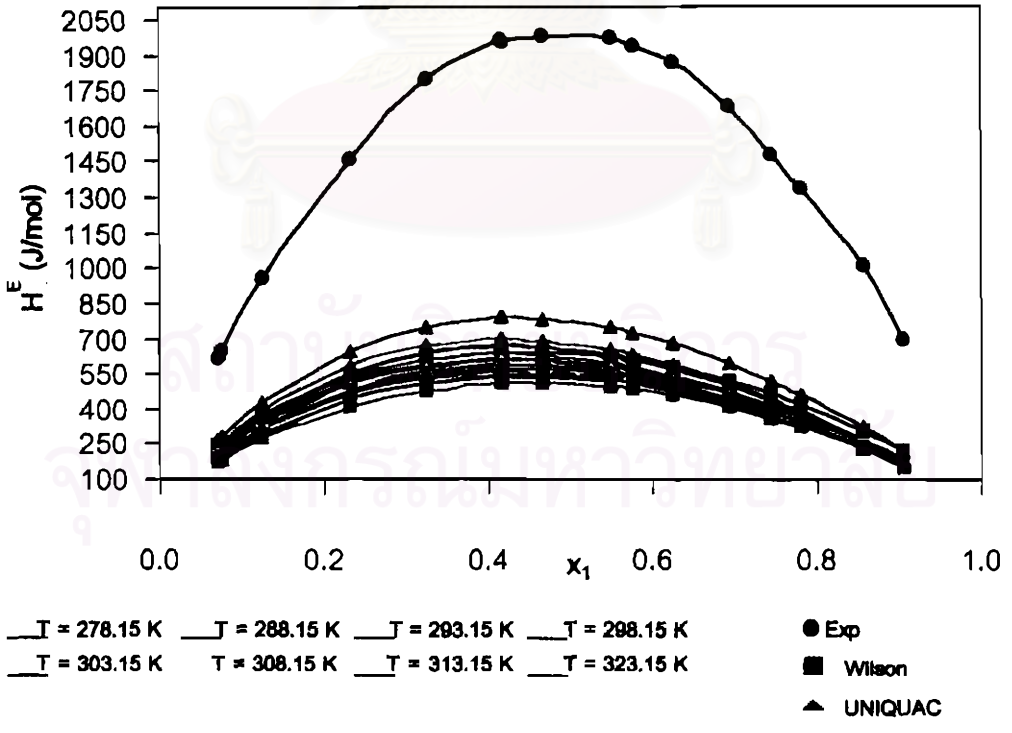

Figure 4.32 H^E (J/mol) of butanenitrile (1) and 2-butanol (2) system at 298.15 K based on parameters from VLE data at eight temperatures.

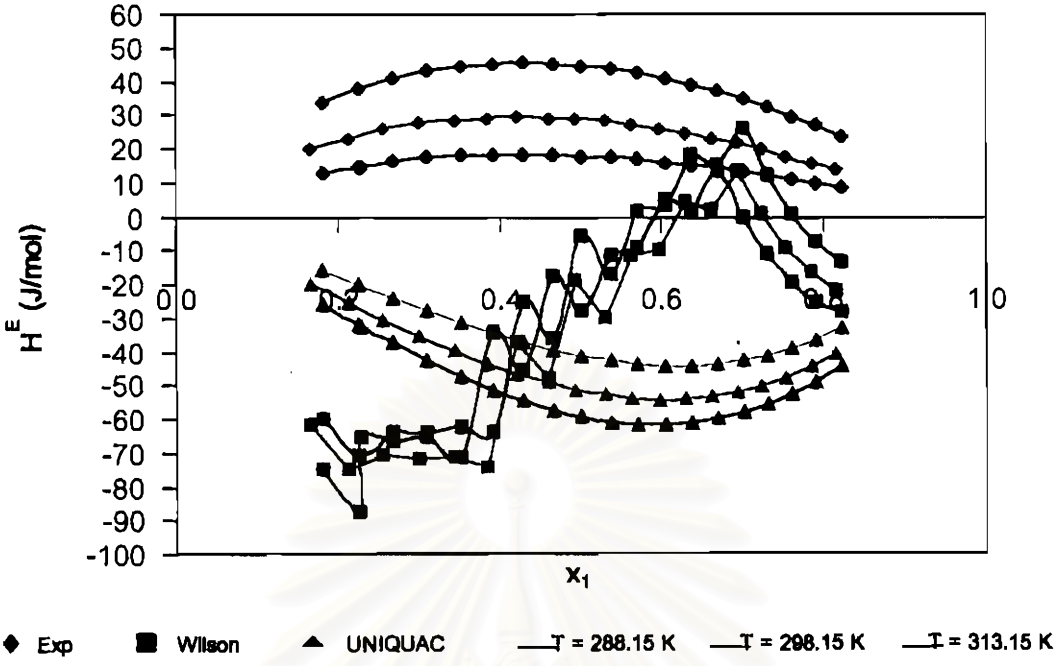

Figure 4.33 H^E (J/mol) of 1-chloropentane (1) and di-n-butyl ether (2) system based on parameters from VLE data at 313.15 K.

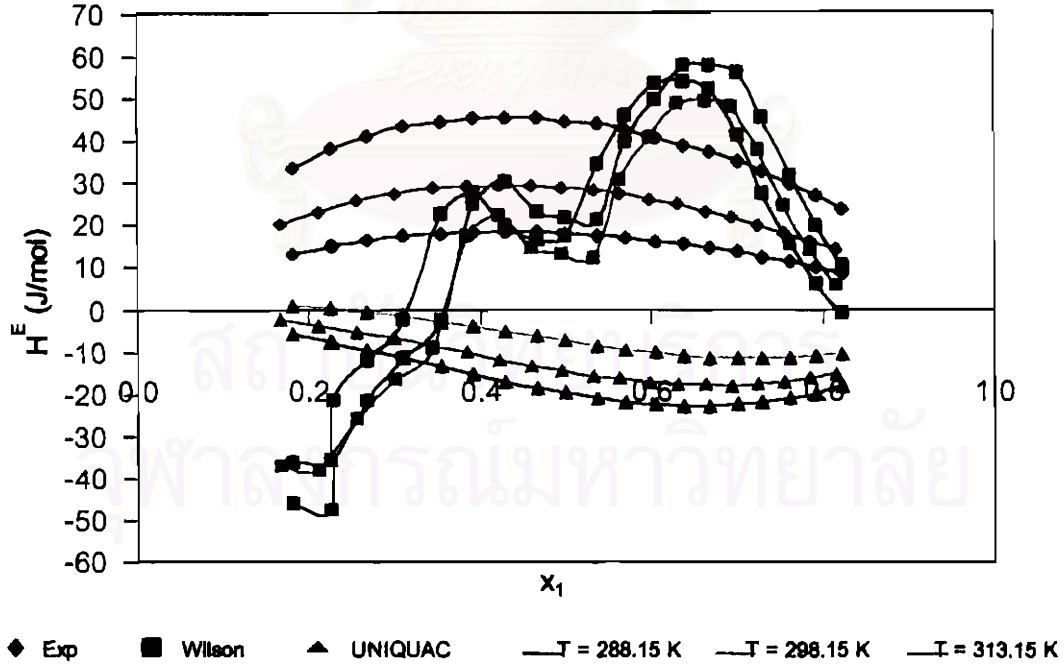

Figure 4.34 H^E (J/mol) of 1-chloropentane (1) and di-n-butyl ether (2) system based on parameters from VLE data at 313.15 K.

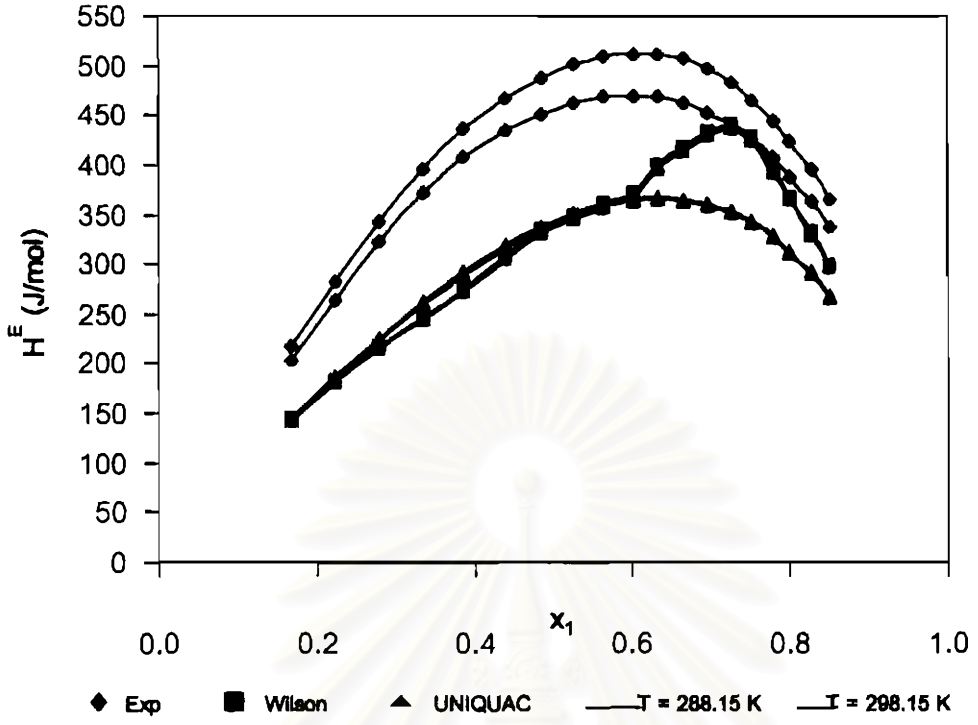

Figure 4.35 H^E (J/mol) of 1,2-dichloroethane (1) and di-n-butyl ether (2) system based on parameters from VLE data at 330.00 K.

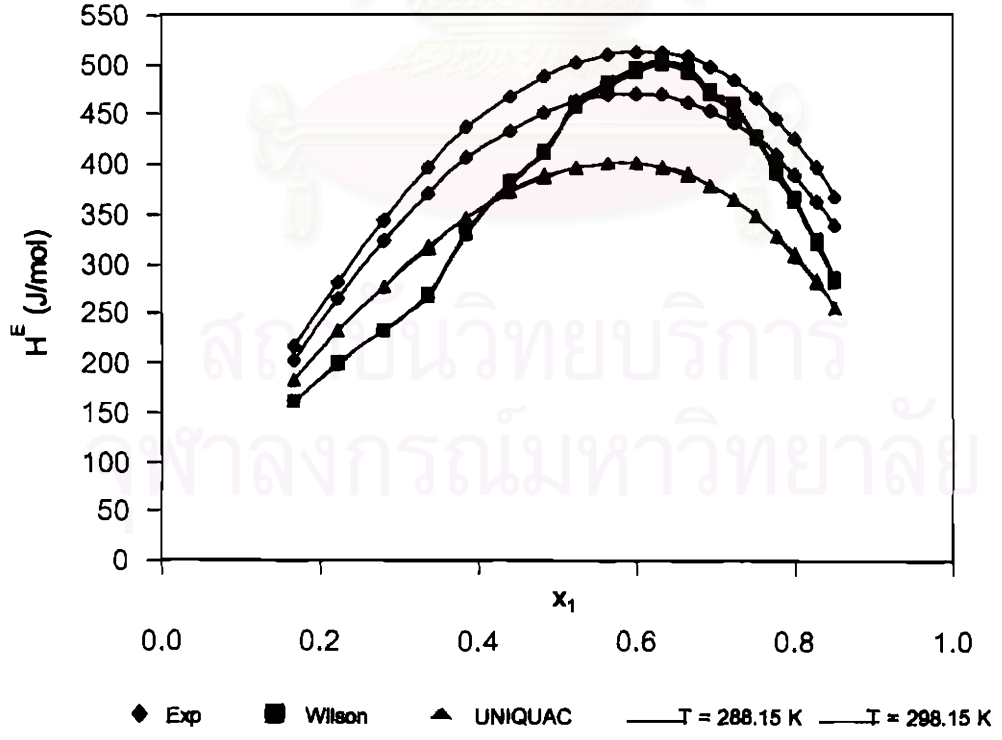

Figure 4.36 H^E (J/mol) of 1,2-dichloroethane (1) and di-n-butyl ether (2) system based on parameters from VLE data at 350.00 K.

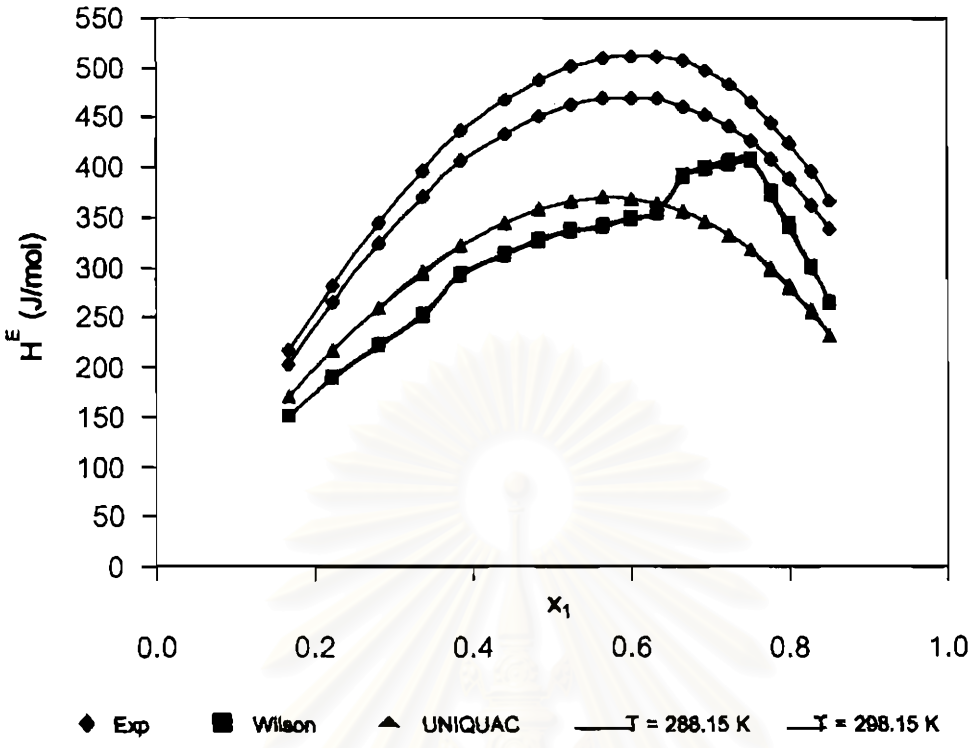

Figure 4.37 H^E (J/mol) of 1,2-dichloroethane (1) and di-n-butyl ether (2) system based on parameters from VLE data at 370.00 K.

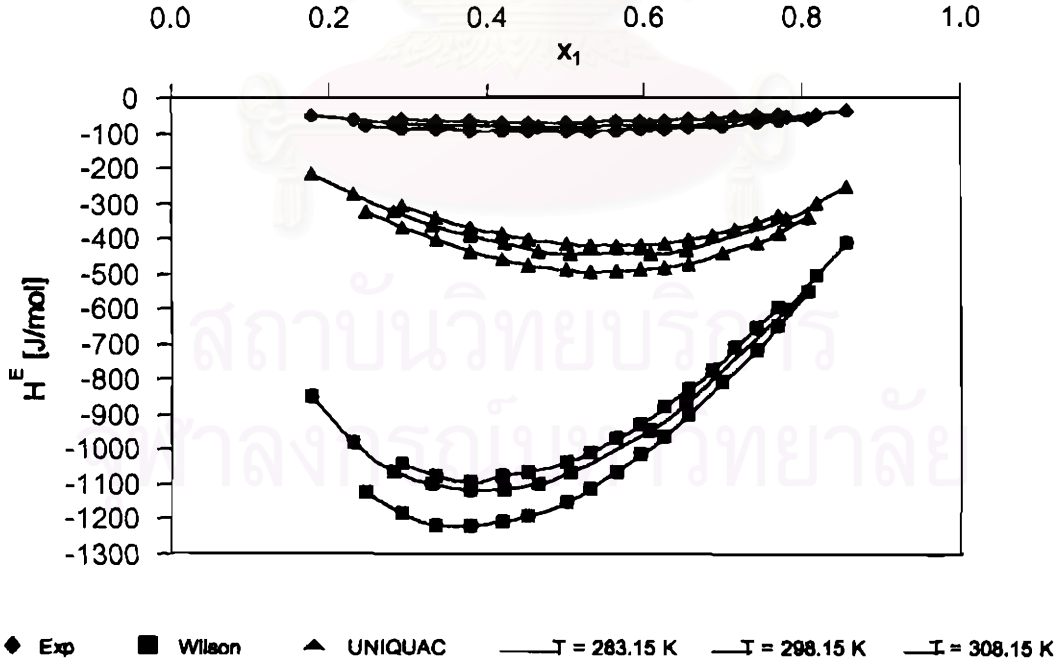

Figure 4.38 H^E (J/mol) of 1,1,1-trichloroethane (1) and di-n-butyl ether (2) system based on parameters from VLE data at 323.15 K.

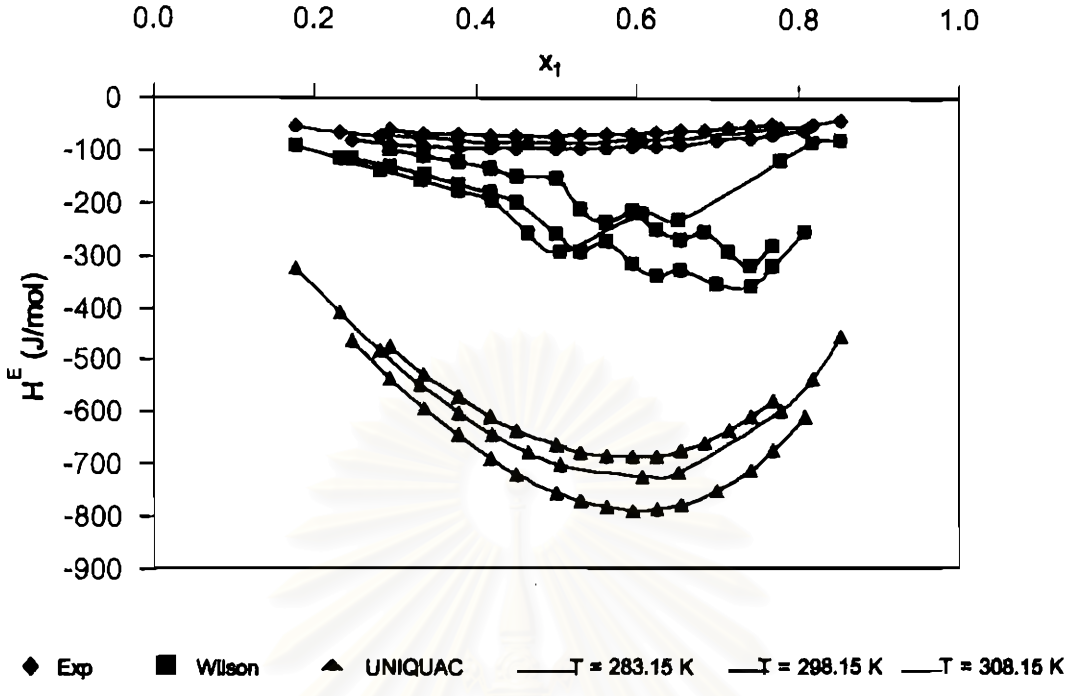

Figure 4.39 H^E (J/mol) of 1,1,1-trichloroethane (1) and di-n-butyl ether (2) system based on parameters from VLE data at 343.15 K.

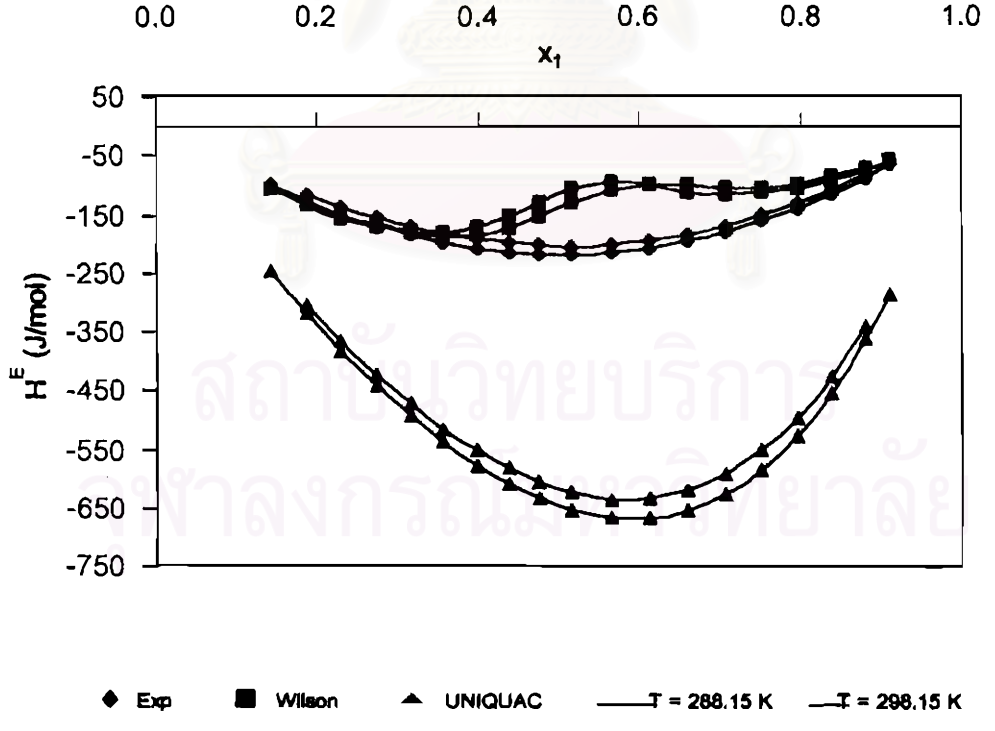

Figure 4.40 H^E (J/mol) of toluene (1) and 1-chlorohexane (2) system based on parameters from VLE data at 323.15 K.

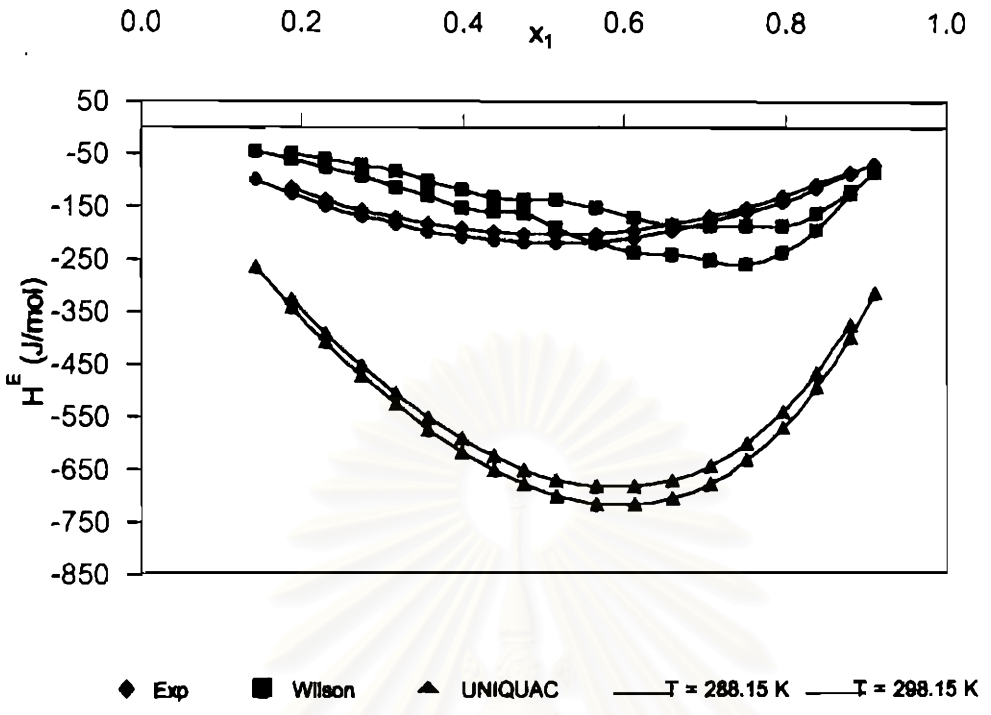

Figure 4.41 H^E (J/mol) of toluene (1) and 1-chlorohexane (2) system based on parameters from VLE data at 343.15 K.

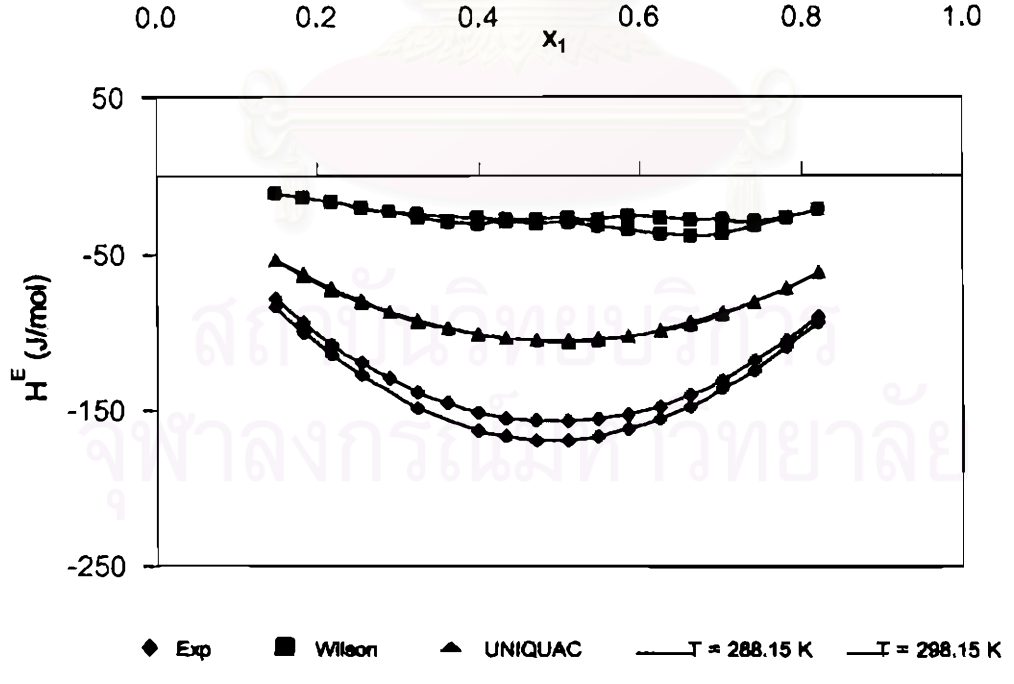

Figure 4.42 H^E (J/mol) of 1-chlorohexane (1) and ethylbenzene (2) system based on parameters from VLE data at 323.15 K.

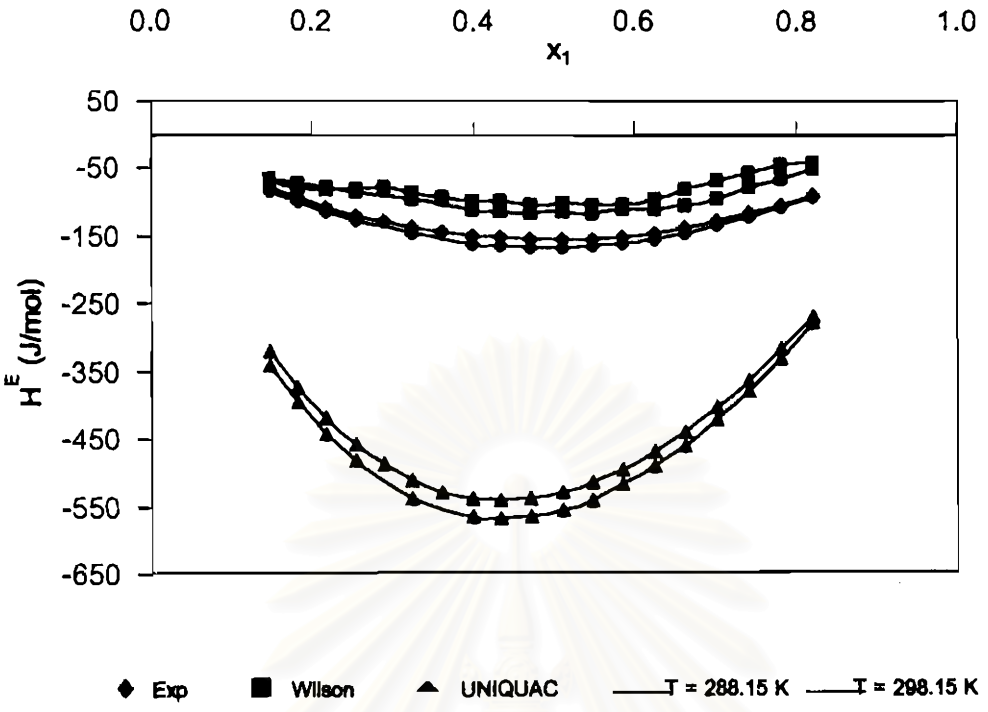

Figure 4.43 H^E (J/mol) of 1-chlorohexane (1) and ethylbenzene (2) system based on parameters from VLE data at 343.15 K.

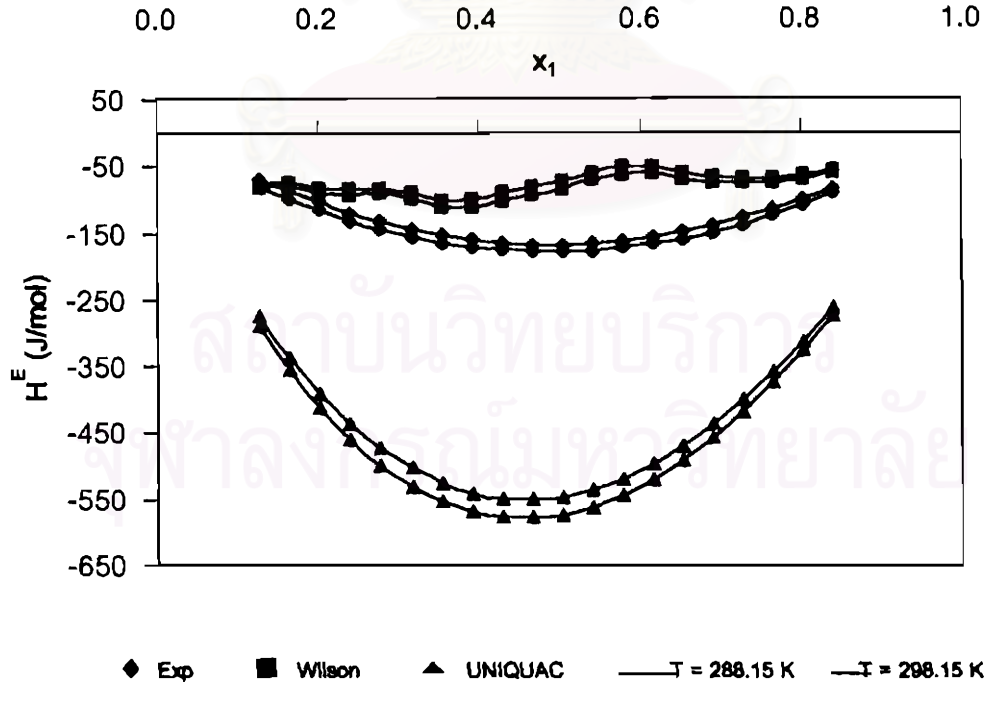

Figure 4.44 H^E (J/mol) of 1-chlorohexane (1) and n-propylbenzene (2) system based on parameters from VLE data at 363.15 K.

4.4 Calculated saturation pressure based on parameters from H^E data

On the other hand, the calculated pressure values based on the fitted Wilson and UNIQUAC parameters (Table 4.4) are presented in Figures 4.45 - 4.74. Moreover, the percent average absolute deviations of the pressures, %AAD (P) are reported in Table 4.6. The table also indicates that the Wilson equation gives better results than the UNIQUAC equation for mixtures of 1,2-epoxybutane with alkanols, ethyl formate with benzene, ethyl formate with cyclohexane and butanenitrile with 2-butanol.

The percent average absolute deviations in mixtures of 1-chlorohexane with three n-alkylbenzene, di-n-butyl ether with chlorinated hydrocarbons except with 1,1,1-trichloroethane based on parameters from H^E data at 283.15 K by the UNIQUAC are less than 10%. It indicates that the UNIQUAC equation gives a good fit of these systems.

Table 4.6 %AAD in saturation pressure for thirteen binary systems based on parameters from H^E data.

Systems	No of data	T/K	%AAD (P)	
			Wilson	UNIQUAC
benzene + cyclohexane	35[a, e]	323.15	39.66	20.78
	35[b, e]	323.15	40.55	20.90
	35[c, e]	323.15	36.91	21.03
	35[d, e]	323.15	44.37	20.10
	36[a, e]	333.15	39.29	20.59
	36[b, e]	333.15	40.18	20.70
	36[c, e]	333.15	36.57	20.83
	36[d, e]	333.15	44.01	19.93
1,2-epoxybutane + methanol	24[e]	298.15	7.03	8.22
1,2-epoxybutane + ethanol	25[e]	298.15	33.83	45.72
1,2-epoxybutane + 2-propanol	24[e]	298.15	63.72	111.87
ethyl formate + benzene	10[e]	323.15	6.63	11.33
	10[f]	323.15	4.24	8.73
	10[g]	323.15	3.30	7.83
ethyl formate + cyclohexane	9[e]	323.15	29.31	64.83
	9[f]	323.15	33.10	62.42
1-chlorohexane + n-propylbenzene	13[h]	363.15	3.93	2.43
	13[e]	363.15	3.68	2.15
1-chlorohexane + ethylbenzene	16[h]	323.15	3.32	1.64
	16[e]	323.15	3.15	1.29
	18[h]	343.15	3.72	1.93
	18[e]	343.15	3.55	1.56

Table 4.6 (continued)

Systems	No of data	T/K	%AAD (P)	
			Wilson	UNIQUAC
toluene + 1-chlorohexane	13[h]	323.15	5.59	1.72
	13[e]	323.15	5.16	1.69
	16[h]	343.15	4.85	1.41
	16[e]	343.15	4.48	1.39
1-chloropentane + di-n-butyl ether	14[h]	313.15	2.58	0.26
	14[e]	313.15	4.11	0.76
	14[i]	313.15	4.17	1.40
	15[h]	323.15	2.30	0.14
	15[e]	323.15	3.51	0.48
	15[i]	323.15	3.54	1.01
1,2-dichloroethane + di-n-butyl ether	14[h]	330.00	17.81	4.05
	14[e]	330.00	25.02	5.96
	16[h]	350.00	8.58	1.65
	16[e]	350.00	12.25	2.69
	15[h]	370.00	11.55	3.02
	15[e]	370.00	16.54	4.54
1,1,1-trichloroethane + di-n-butyl ether	19[j]	323.15	7.03	18.98
	19[e]	323.15	6.86	1.78
	19[f]	323.15	7.00	1.83
	21[j]	343.15	6.12	16.04
	21[e]	343.15	5.99	2.02
	21[f]	343.15	6.09	2.06

Table 4.6 (continued)

Systems	No of data	T/K	%AAD (P)	
			Wilson	UNIQUAC
butanenitrile + 2-butanol	20[e]	278.15	32.95	232.99
	20[e]	288.15	37.65	224.33
	20[e]	293.15	40.11	220.60
	20[e]	298.15	41.55	215.58
	20[e]	303.15	42.82	210.34
	20[e]	308.15	43.67	204.87
	20[e]	313.15	45.06	200.93
	20[e]	323.15	47.19	193.10

[a] Kuus et al., 1996.

[b] Stokes et al., 1969.

[c] Hsu et al., 1975.

[d] Meyer et al., 1977.

[e] parameters from H^E data at 298.15 K.

[f] parameters from H^E data at 308.15 K.

[g] parameters from H^E data at 318.15 K.

[h] parameters from H^E data at 288.15 K.

[i] parameters from H^E data at 313.15 K.

[j] parameters from H^E data at 283.15 K.

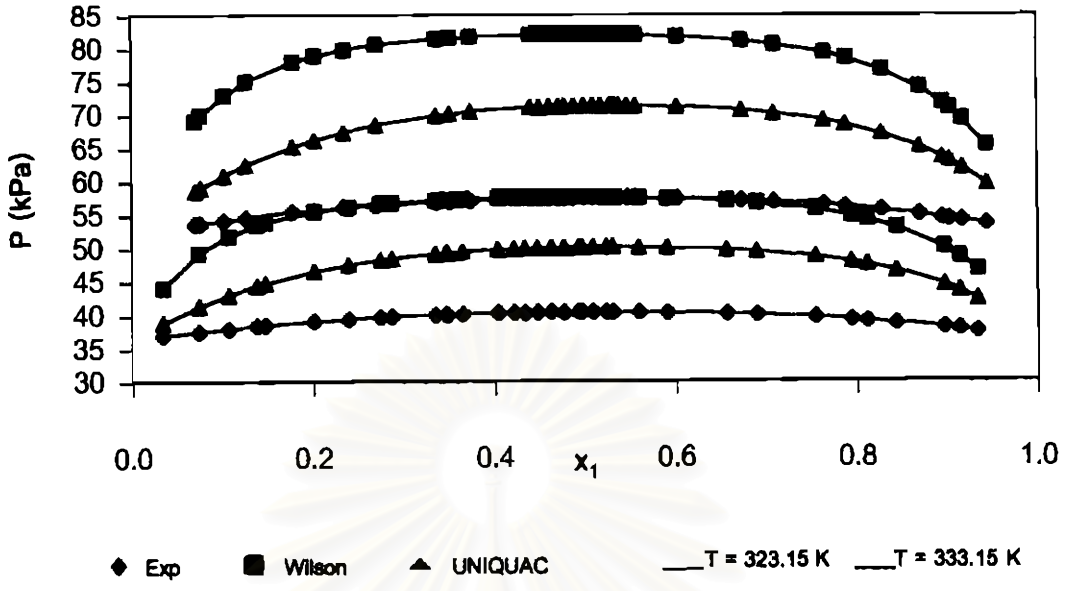

Figure 4.45 P (kPa) of benzene (1) and cyclohexane (2) system based on parameters from H^E data at 298.15 K (Kuus et al., 1996).

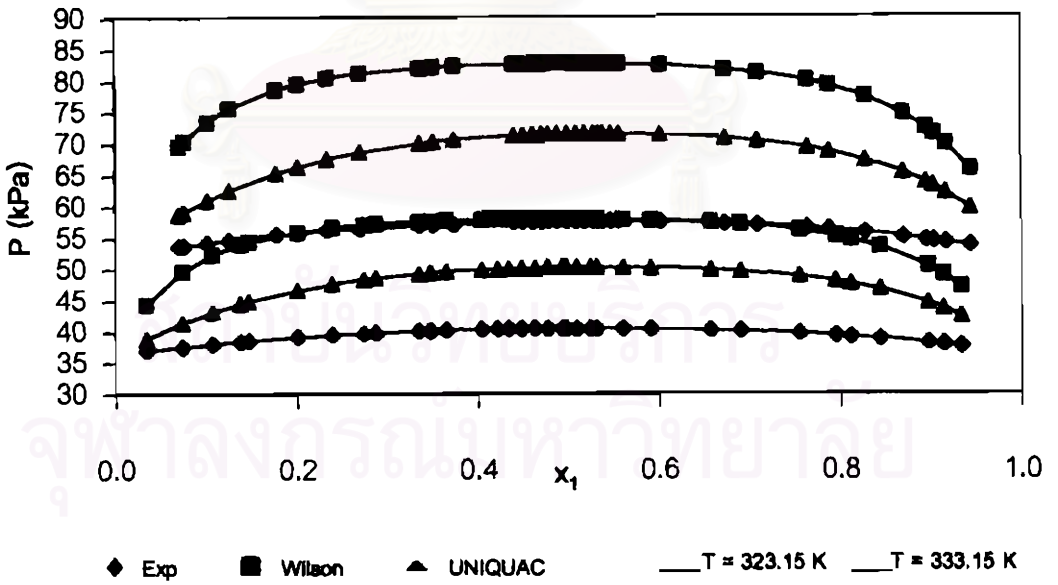

Figure 4.46 P (kPa) of benzene (1) and cyclohexane (2) system based on parameters from H^E data at 298.15 K (Stokes et al., 1969).

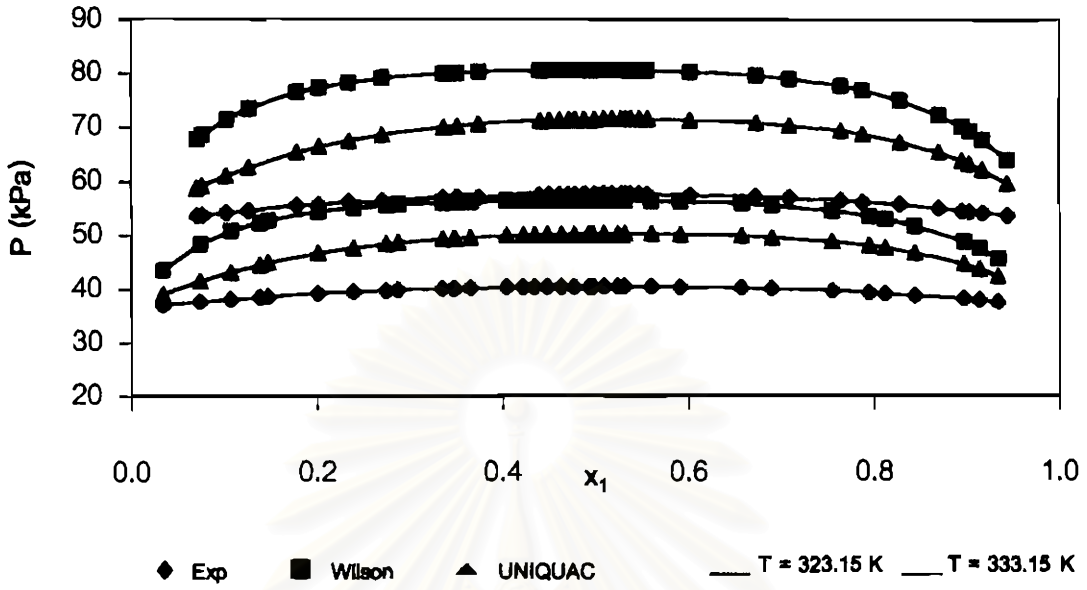

Figure 4.47 P (kPa) of benzene (1) and cyclohexane (2) system based on parameters from H^E data at 298.15 K (Hsu et al., 1975).

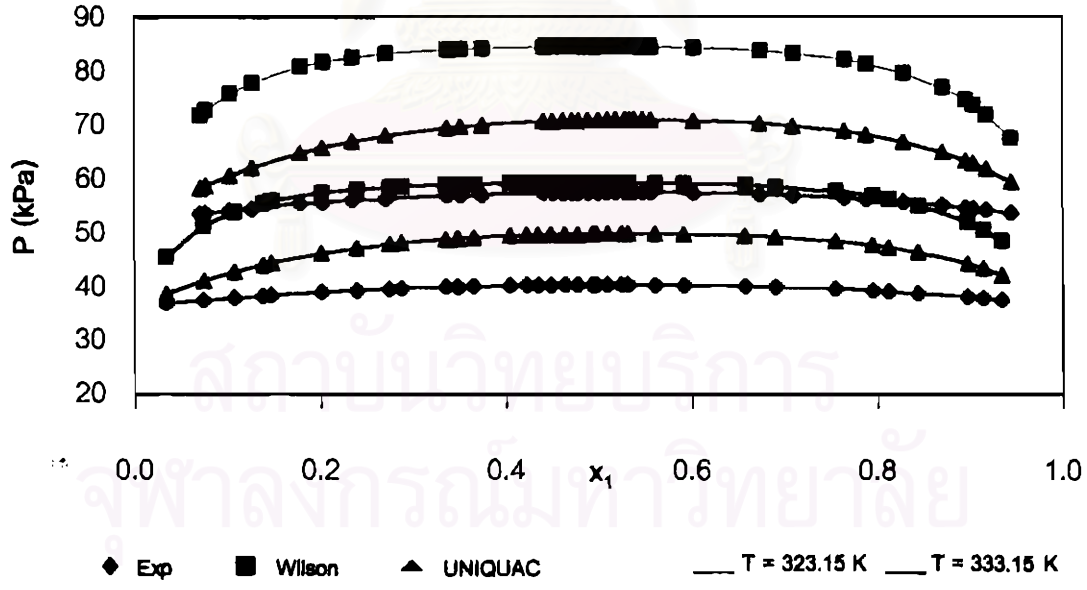

Figure 4.48 P (kPa) of benzene (1) and cyclohexane (2) system based on parameters from H^E data at 298.15 K (Meyer et al., 1977).

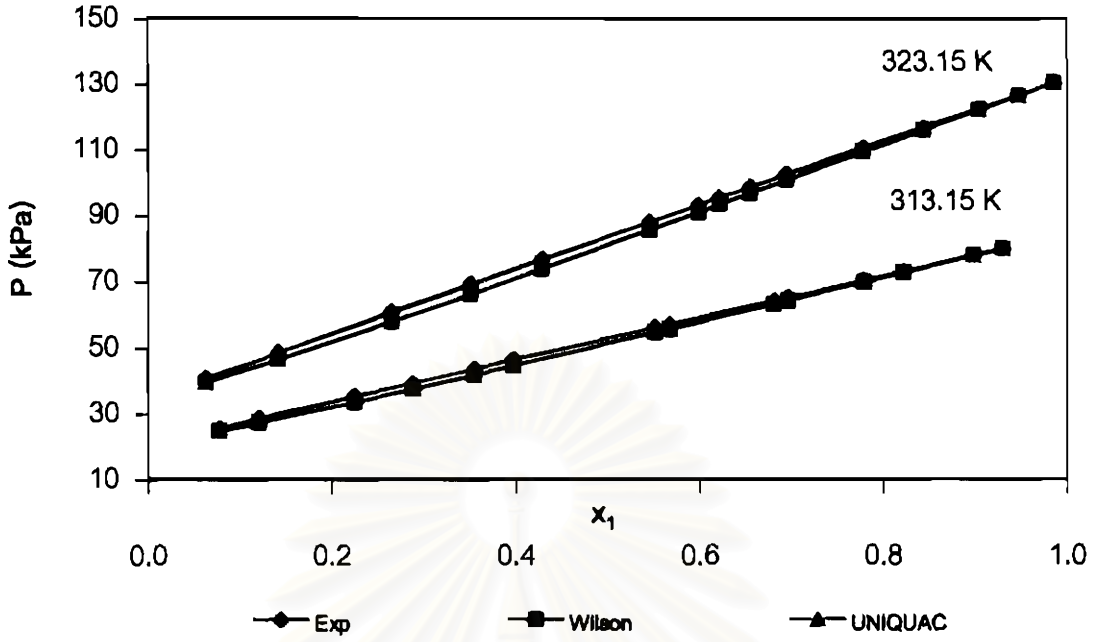

Figure 4.49 P (kPa) of 1-chloropentane (1) and di-n-butyl ether (2) system based on parameters from H^E data at 288.15 K.

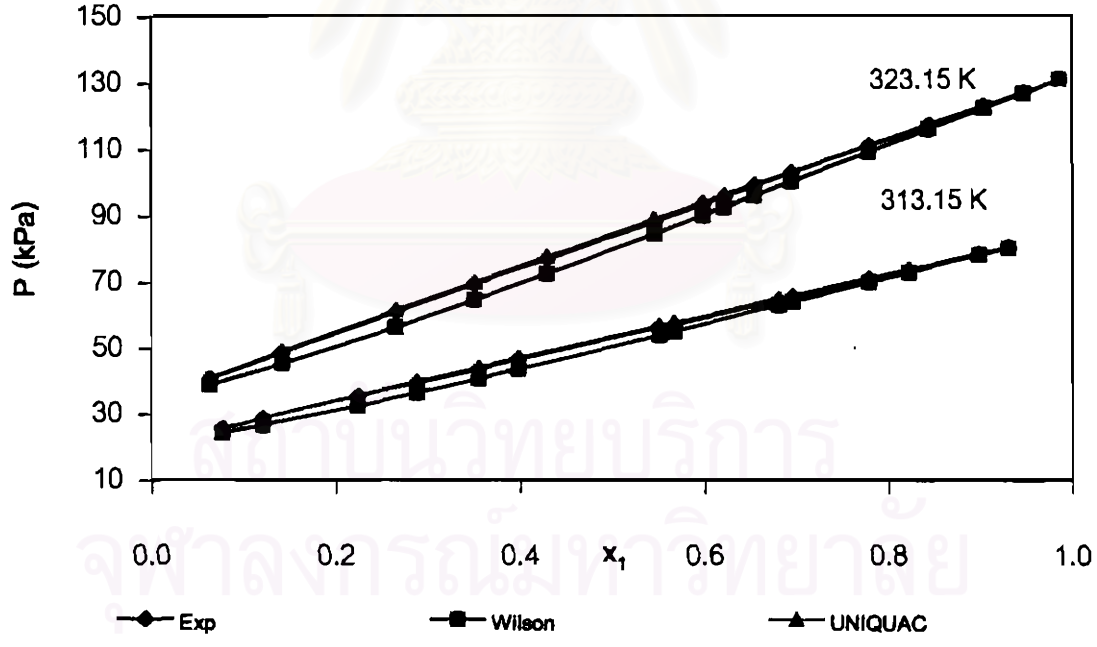

Figure 4.50 P (kPa) of 1-chloropentane (1) and di-n-butyl ether (2) system based on parameters from H^E data at 298.15 K.

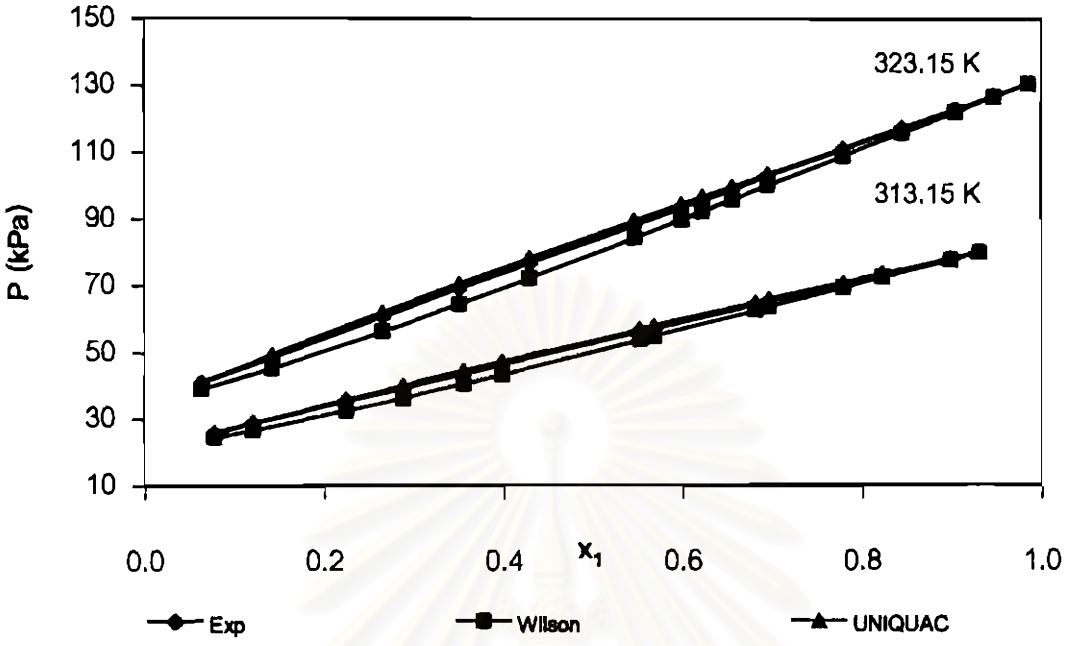

Figure 4.51 P (kPa) of 1-chloropentane (1) and di-n-butyl ether (2) system based on parameters from H^E data at 313.15 K.

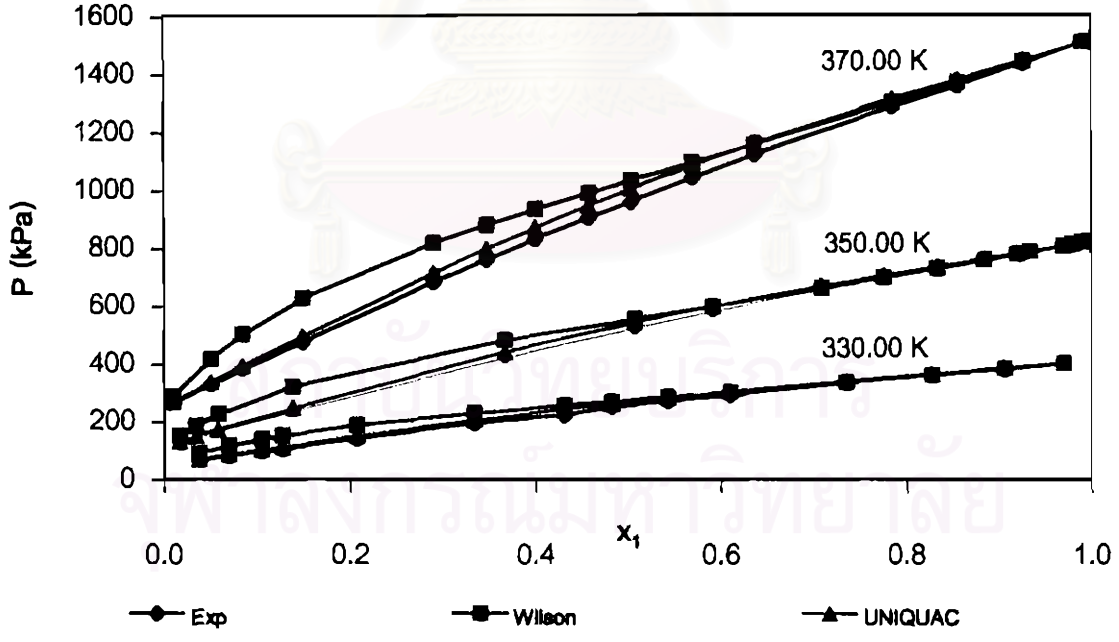

Figure 4.52 P (kPa) of 1,2-dichloroethane (1) and di-n-butyl ether (2) system based on parameters from H^E data at 288.15 K.

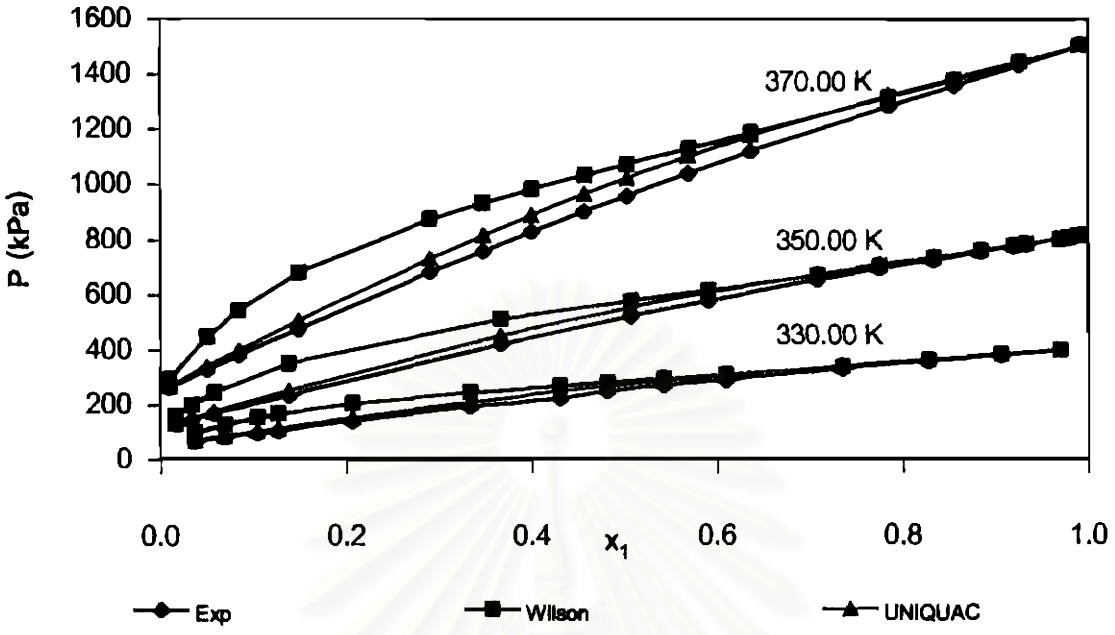

Figure 4.53 P (kPa) of 1,2-dichloroethane (1) and di-n-butyl ether (2) system based on parameters from H^E data at 298.15 K.

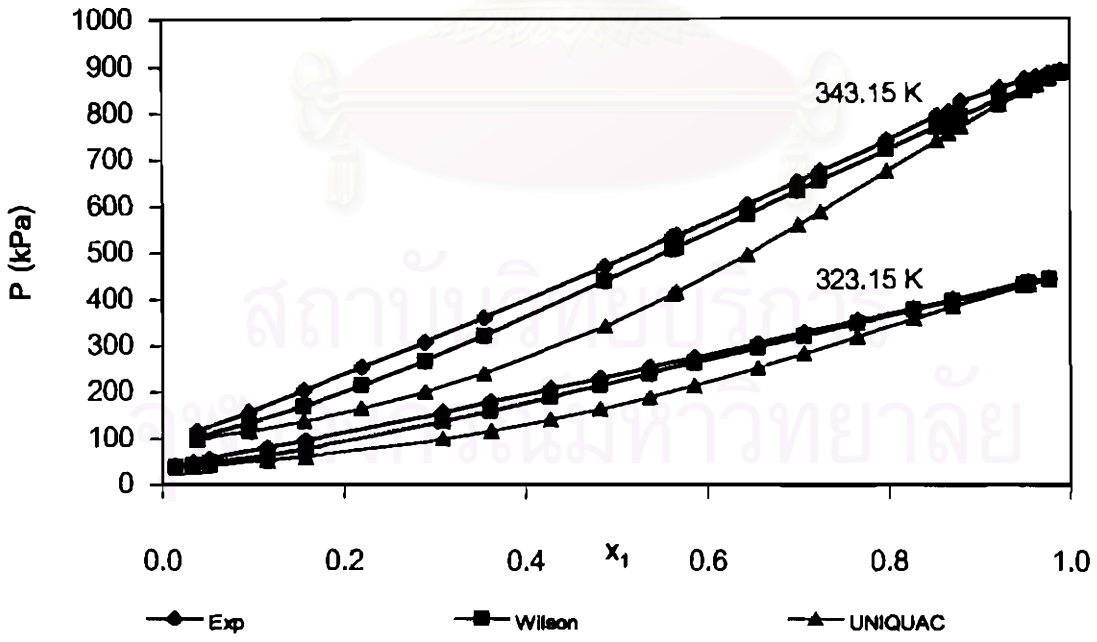

Figure 4.54 P (kPa) of 1,1,1-trichloroethane (1) and di-n-butyl ether (2) system based on parameters from H^E data at 283.15 K.

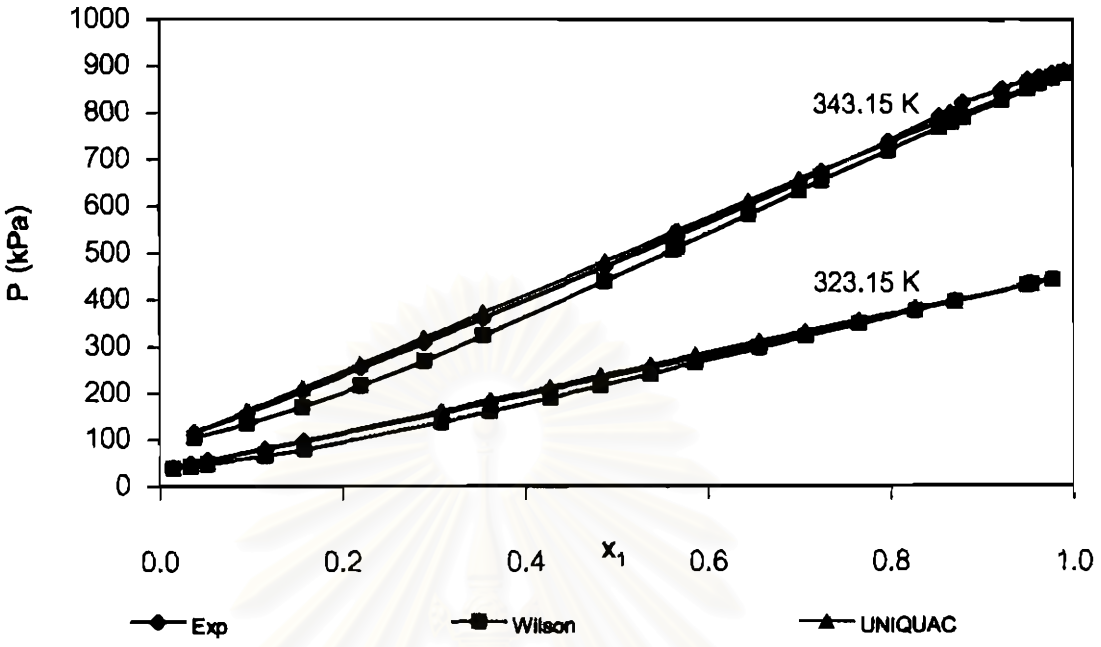

Figure 4.55 P (kPa) of 1,1,1-trichloroethane (1) and di-n-butyl ether (2) system based on parameters from H^E data at 298.15 K.

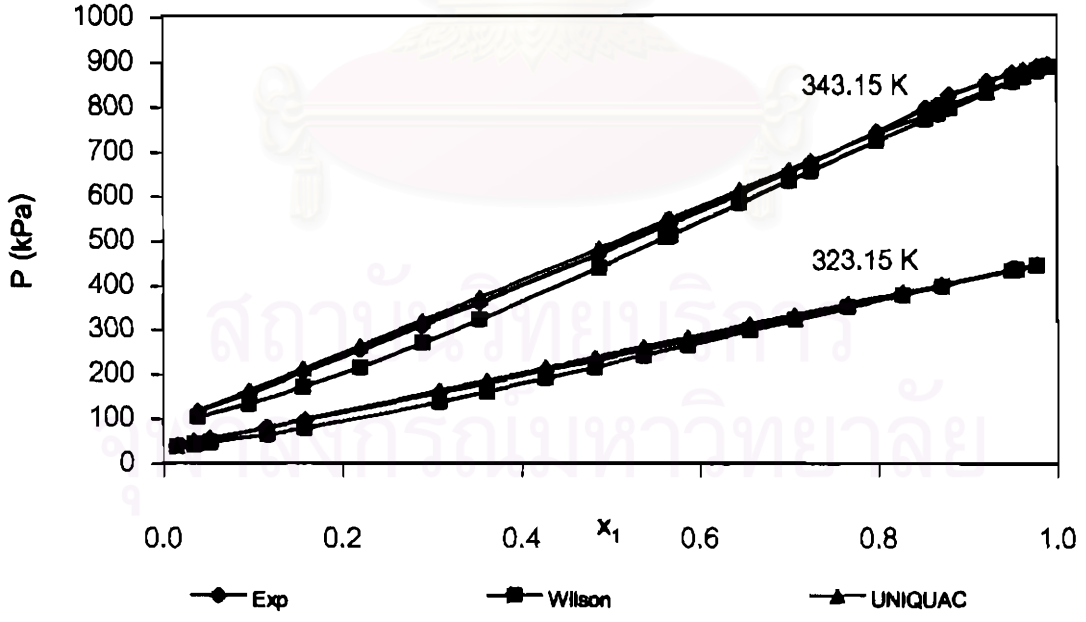

Figure 4.56 P (kPa) of 1,1,1-trichloroethane (1) and di-n-butyl ether (2) system based on parameters from H^E data at 308.15 K.

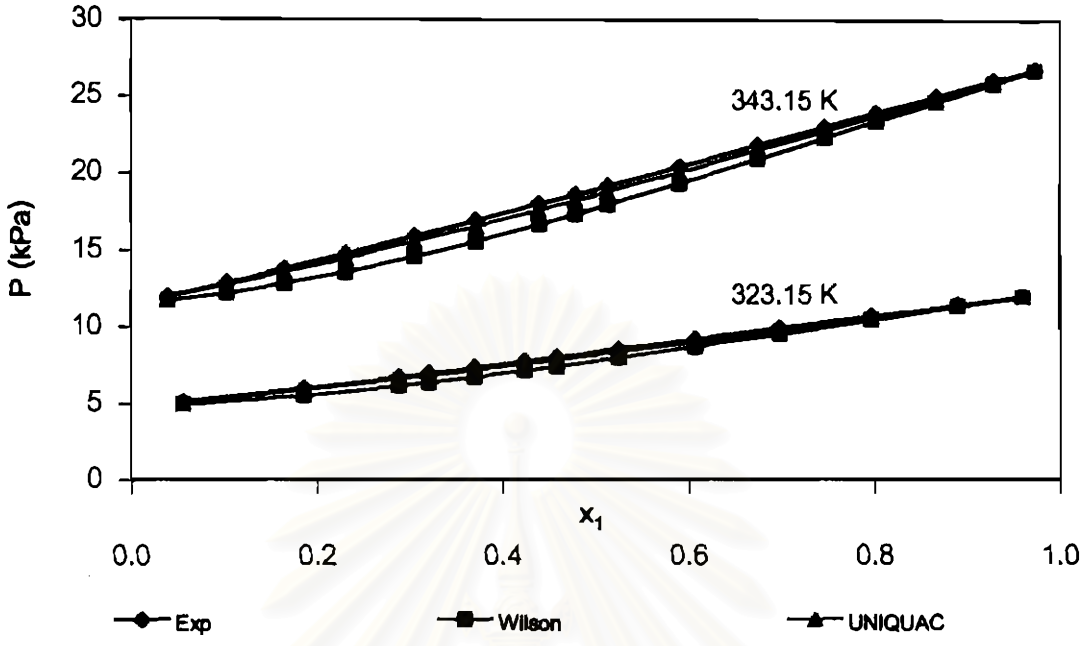

Figure 4.57 P (kPa) of toluene (1) and 1-chlorohexane (2) system based on parameters from H^E data at 288.15 K.

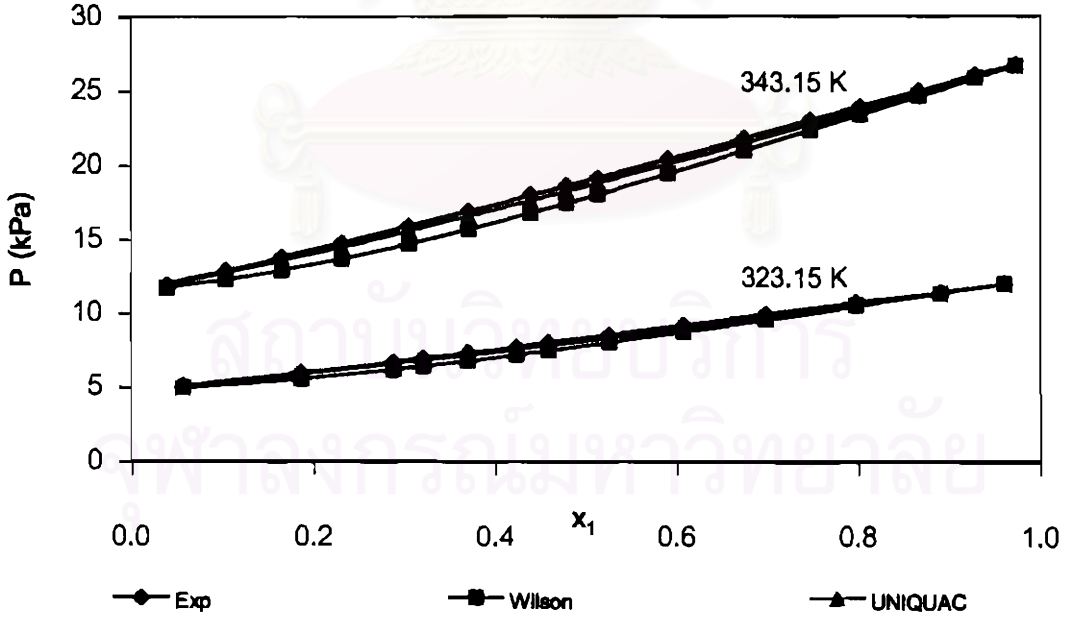

Figure 4.58 P (kPa) of toluene (1) and 1-chlorohexane (2) system based on parameters from H^E data at 298.15 K.

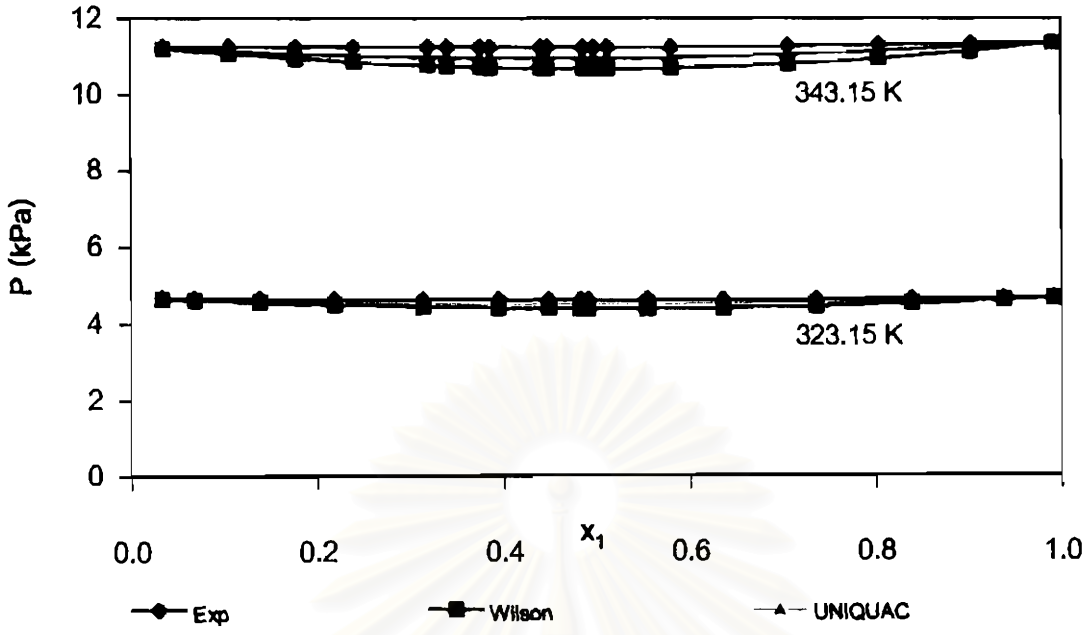

Figure 4.59 P (kPa) of 1-chlorohexane (1) and ethylbenzene (2) system based on parameters from H^E data at 288.15 K.

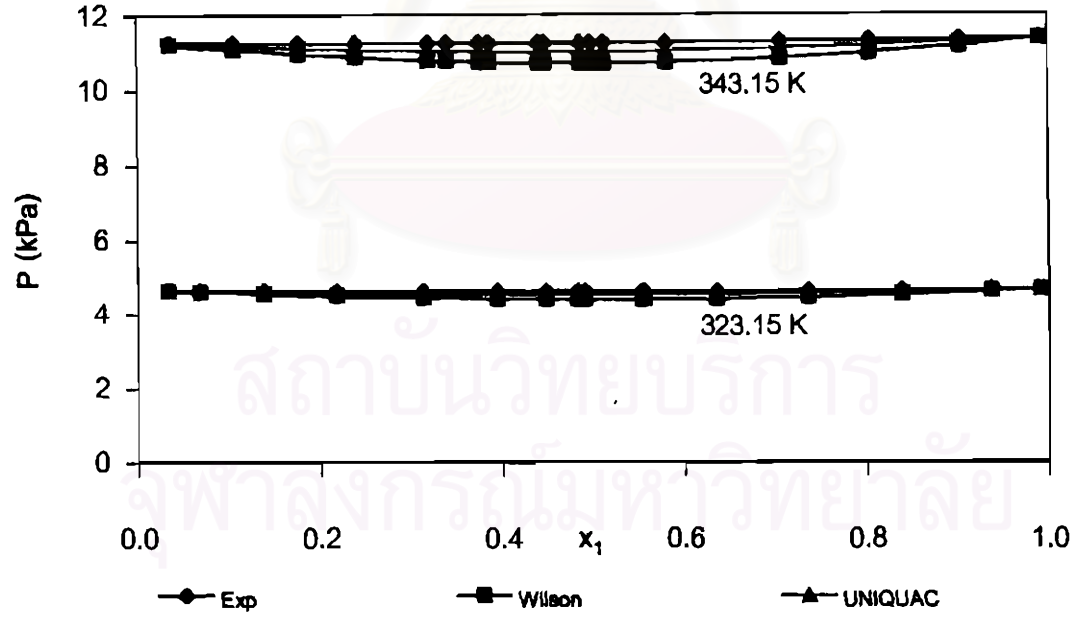

Figure 4.60 P (kPa) of 1-chlorohexane (1) and ethylbenzene (2) system based on parameters from H^E data at 298.15 K.

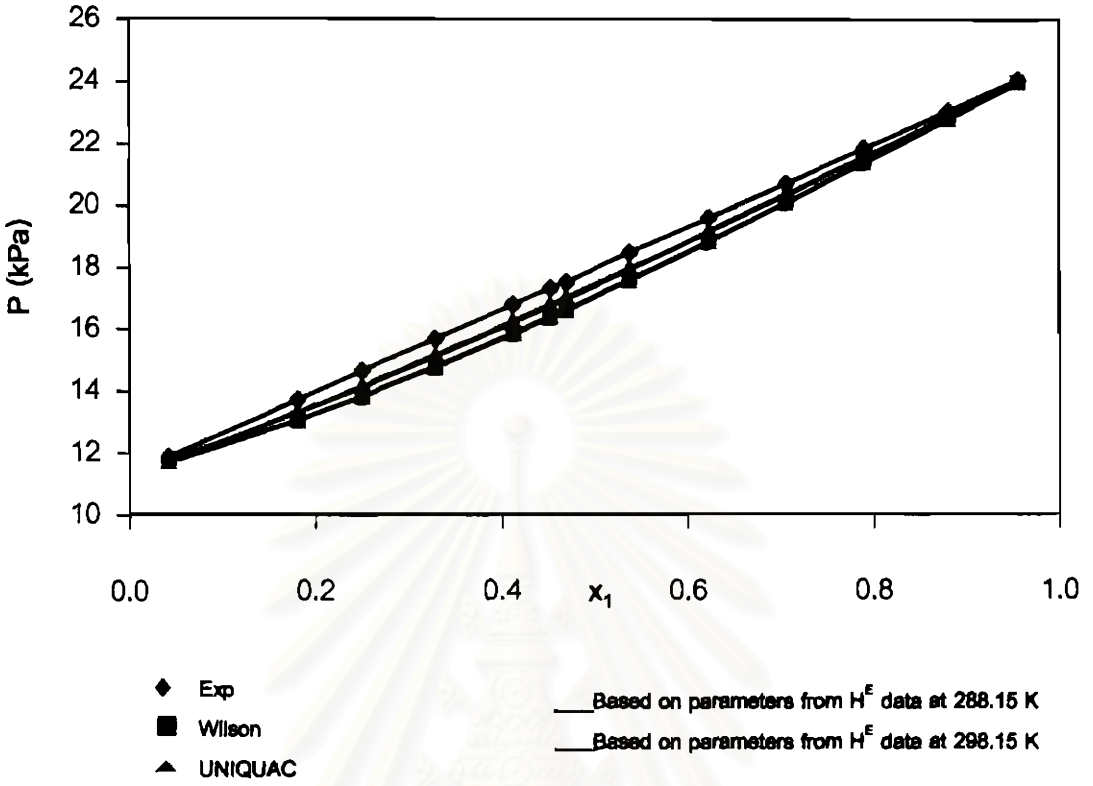

Figure 4.61 P (kPa) of 1-chlorohexane (1) and n-propylbenzene (2) system at 363.15 K based on parameters from H^E data.

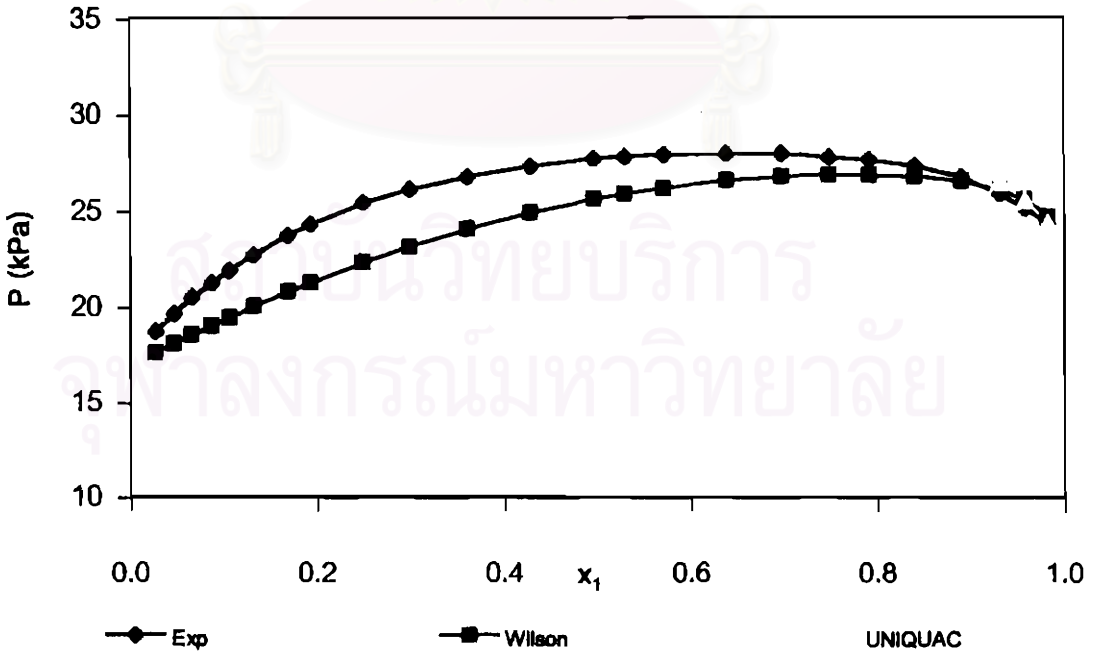

Figure 4.62 P (kPa) of 1,2-epoxybutane (1) and methanol (2) system at 298.15 K based on parameters from H^E data at 298.15 K.

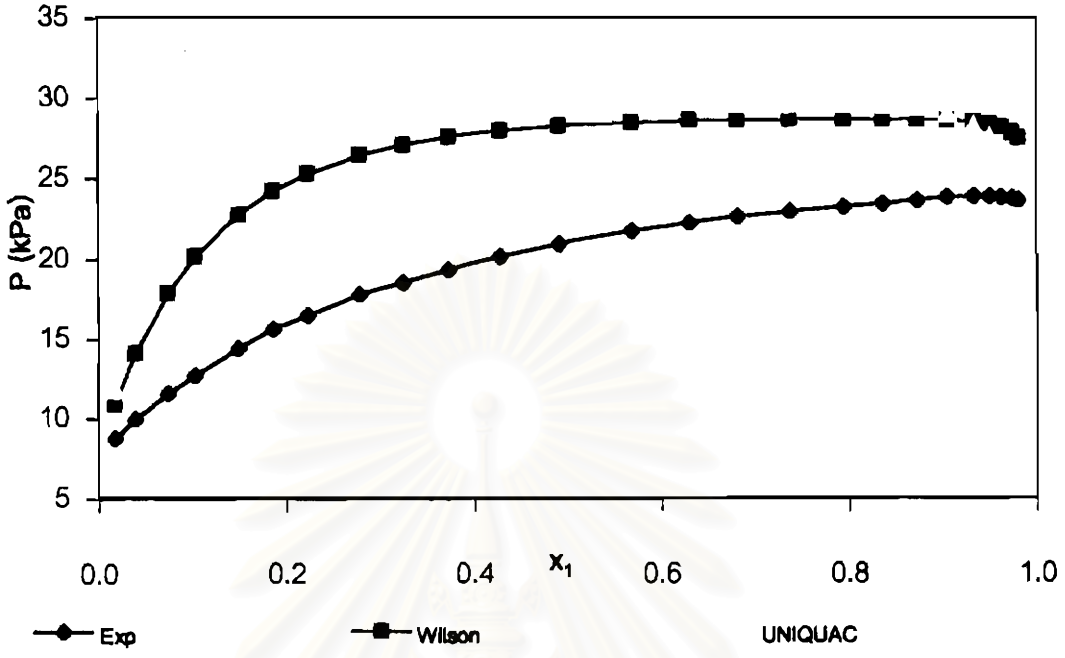

Figure 4.63 P (kPa) of 1,2-epoxybutane (1) and ethanol (2) system at 298.15 K based on parameters from H^E data at 298.15 K.

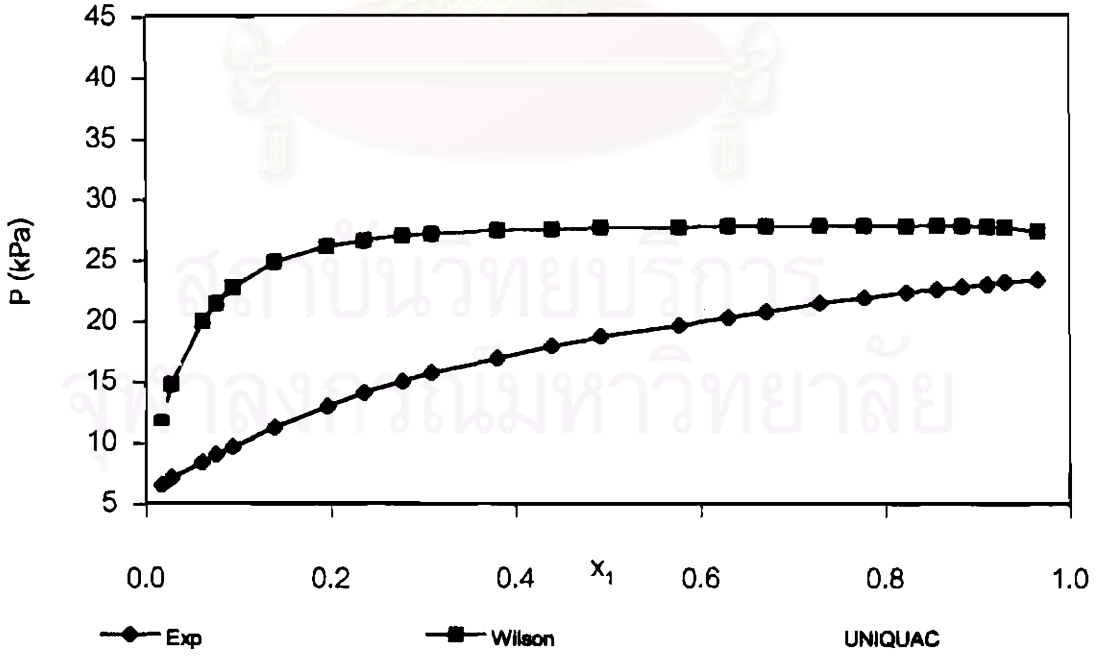

Figure 4.64 P (kPa) of 1,2-epoxybutane (1) and 2-propanol (2) system at 298.15 K based on parameters from H^E data at 298.15 K.

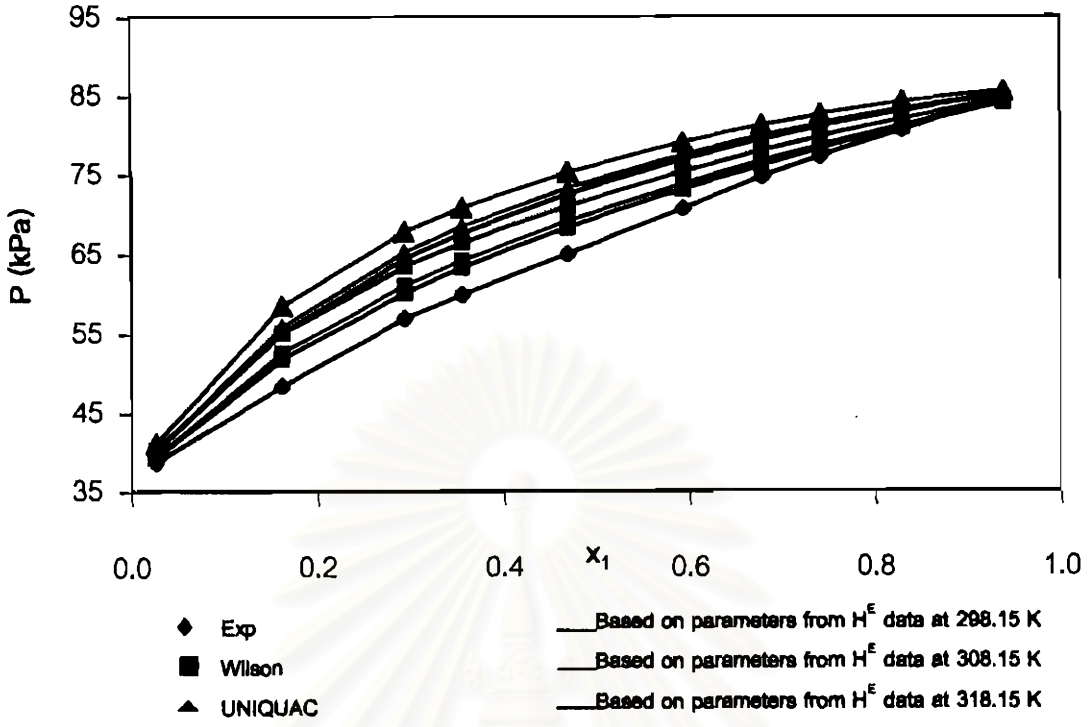

Figure 4.65 P (kPa) of ethyl formate (1) and benzene (2) system at 323.15 K based on H^E data.

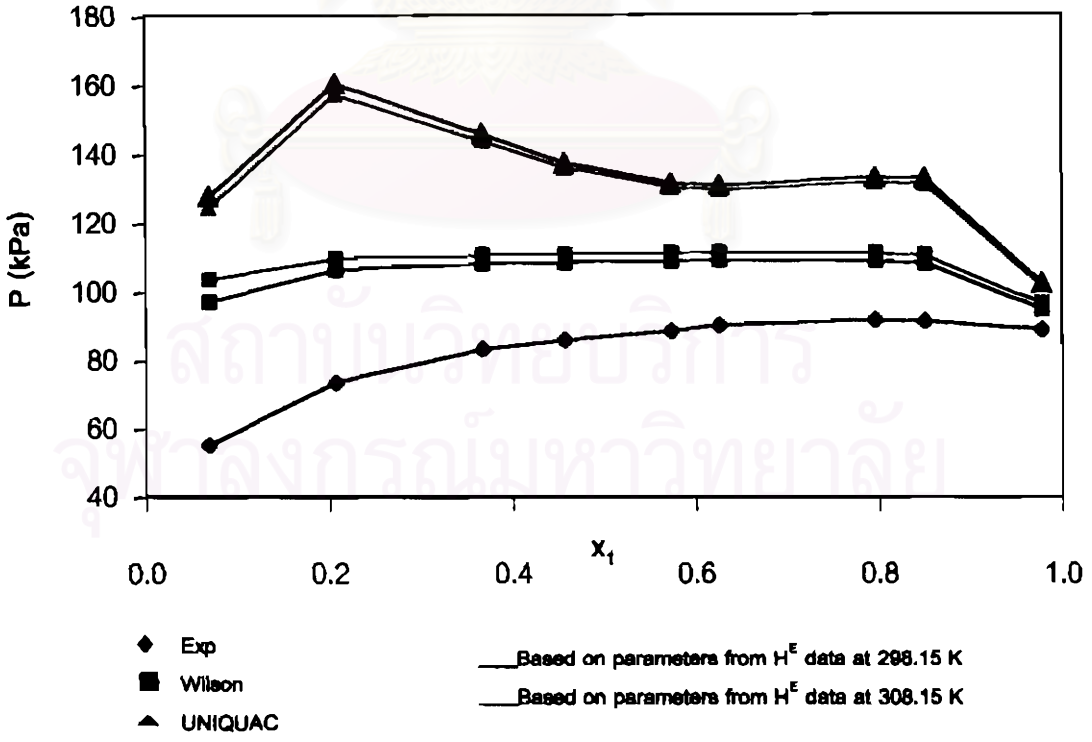

Figure 4.66 P (kPa) of ethyl formate (1) and cyclohexane (2) system at 323.15 K based on H^E data.

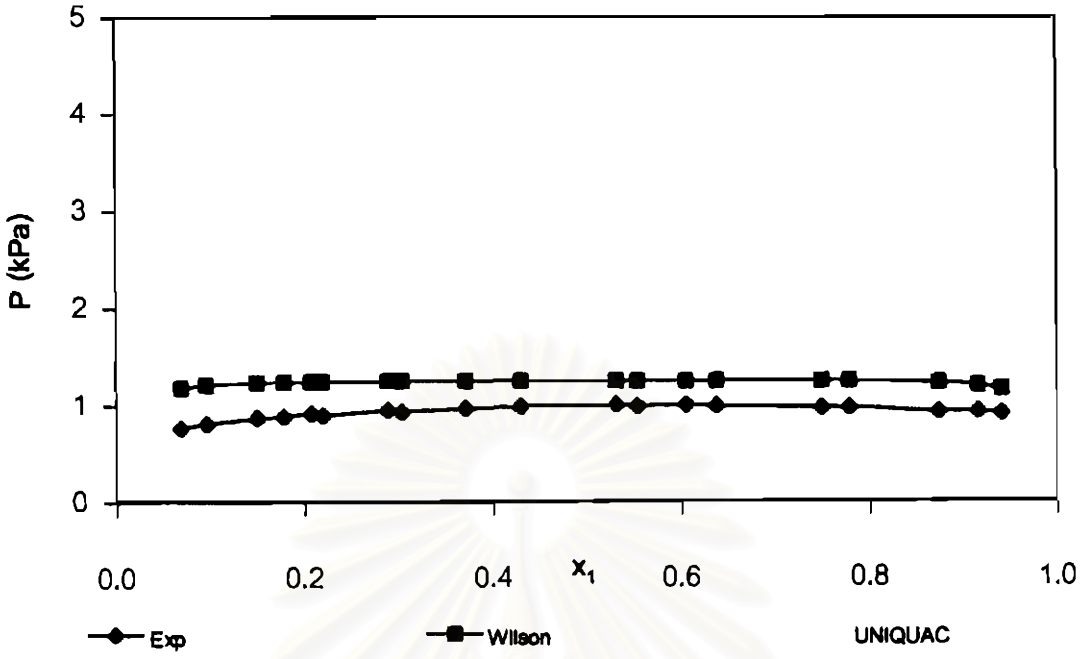

Figure 4.67 P (kPa) of butanenitrile (1) and 2-butanol (2) system at 278.15 K based on parameters from H^E data at 298.15 K.

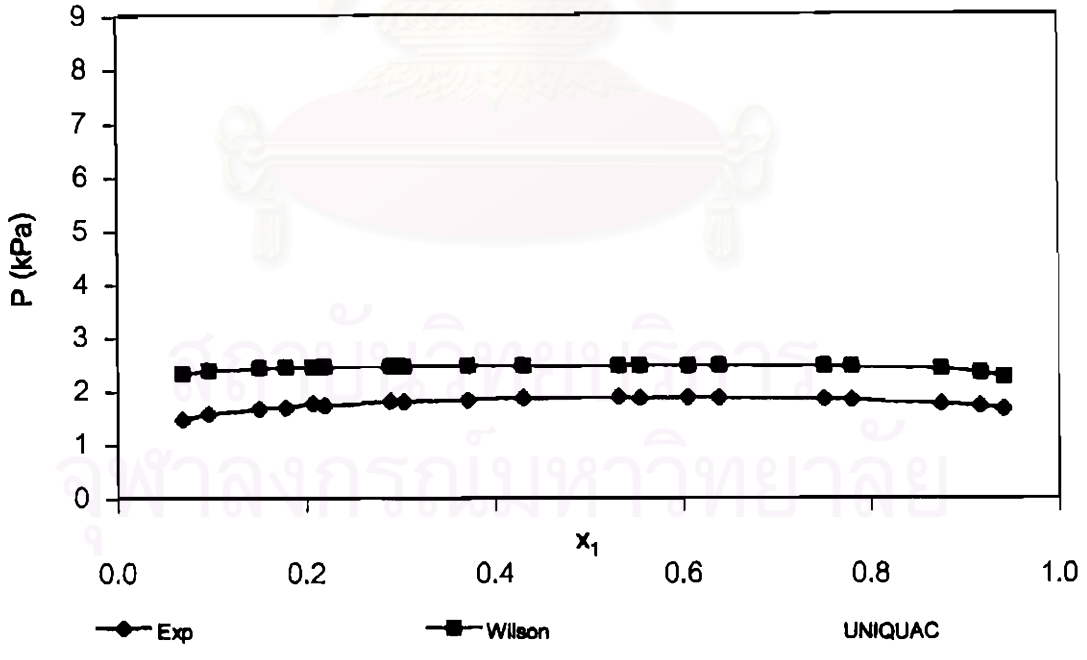

Figure 4.68 P (kPa) of butanenitrile (1) and 2-butanol (2) system at 288.15 K based on parameters from H^E data at 298.15 K.

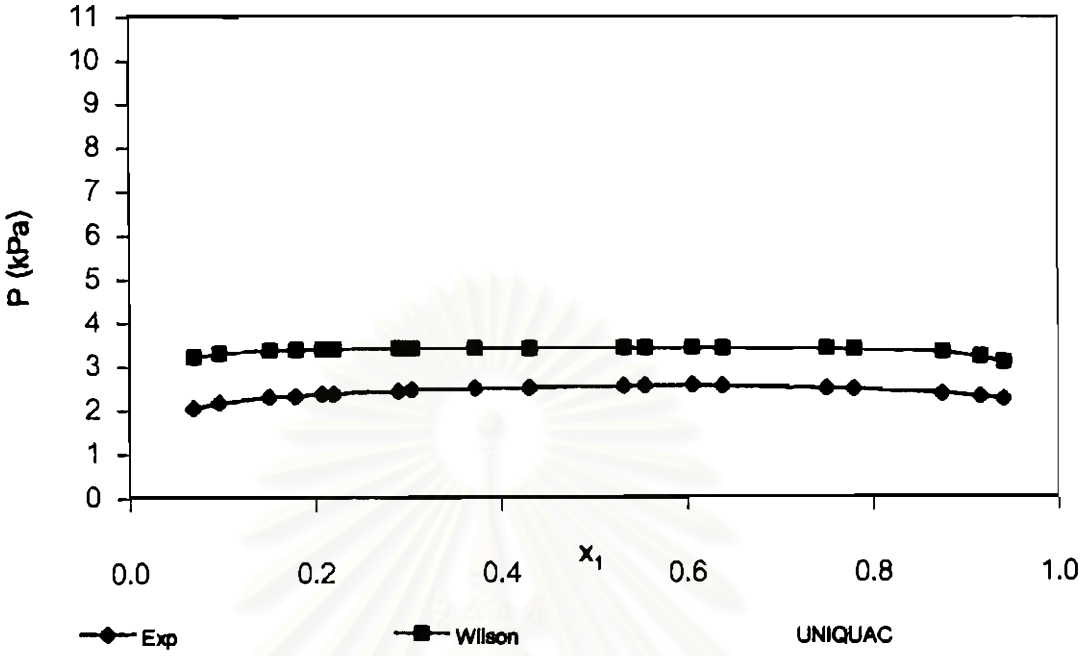

Figure 4.69 P (kPa) of butanenitrile (1) and 2-butanol (2) system at 293.15 K based on parameters from H^E data at 298.15 K.

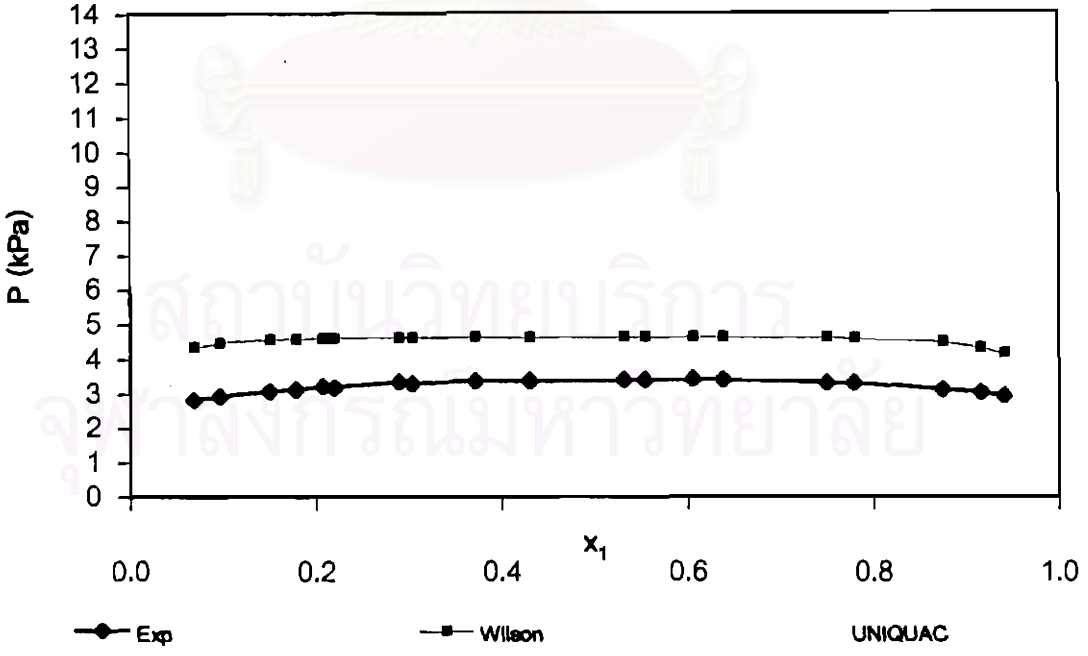

Figure 4.70 P (kPa) of butanenitrile (1) and 2-butanol (2) system at 298.15 K based on parameters from H^E data at 298.15 K.

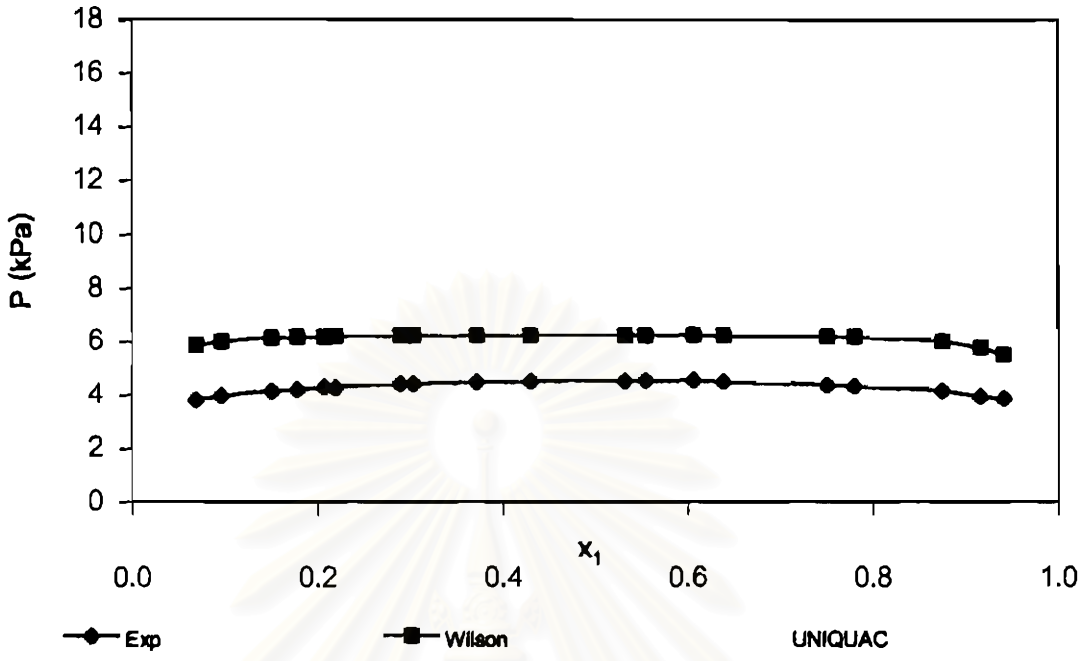

Figure 4.71 P (kPa) of butanenitrile (1) and 2-butanol (2) system at 303.15 K based on parameters from H^E data at 298.15 K.

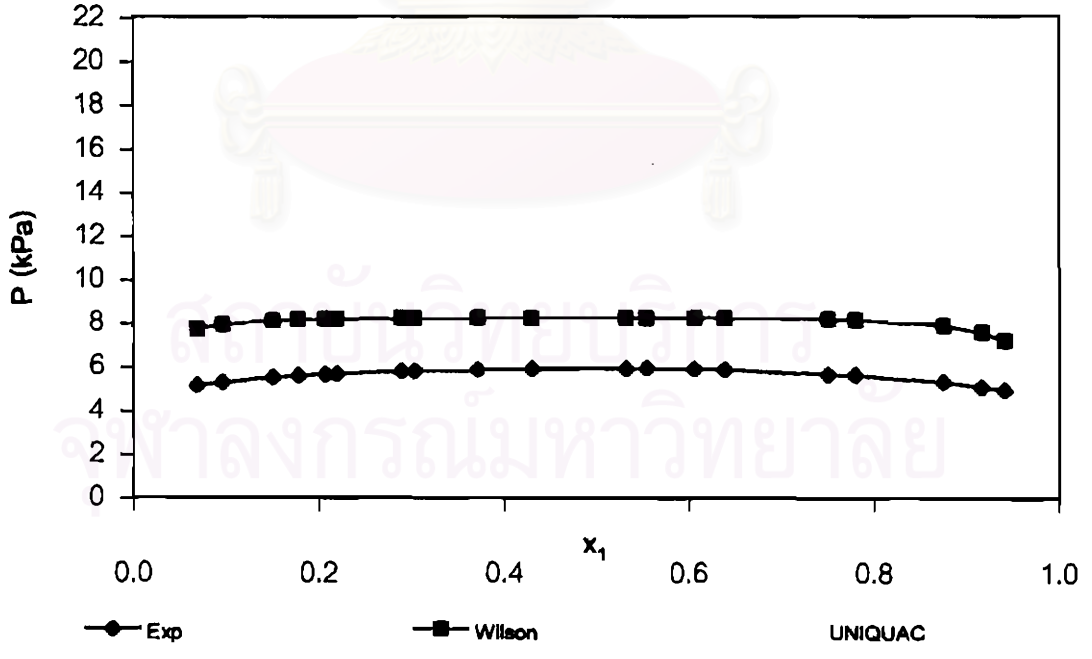

Figure 4.72 P (kPa) of butanenitrile (1) and 2-butanol (2) system at 308.15 K based on parameters from H^E data at 298.15 K.

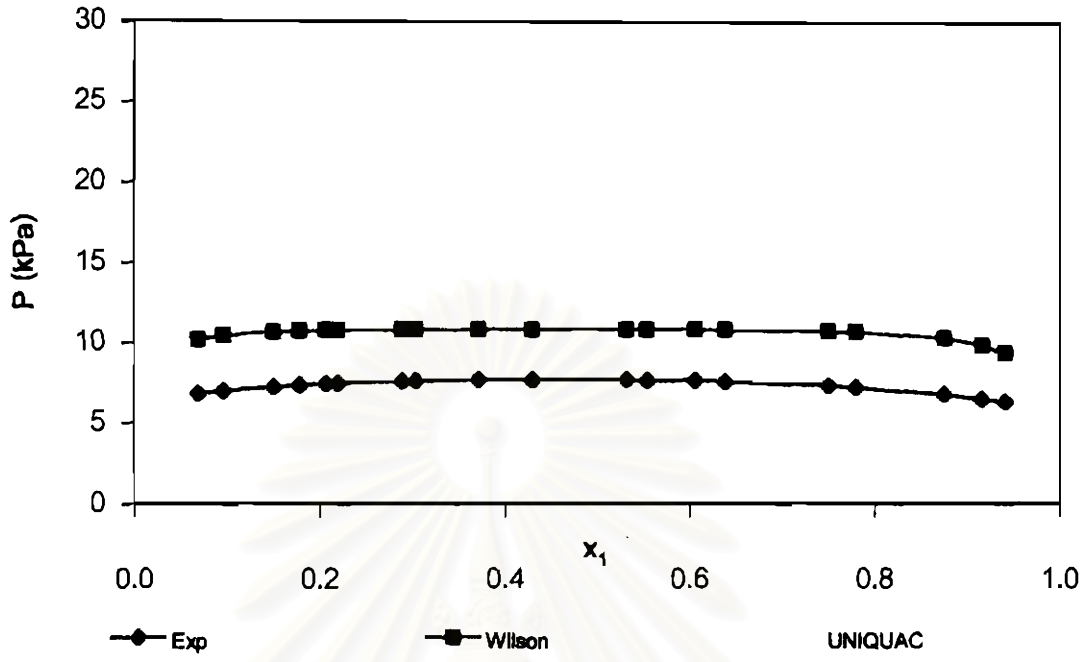

Figure 4.73 P (kPa) of butanenitrile (1) and 2-butanol (2) system at 313.15 K based on parameters from H^E data at 298.15 K.

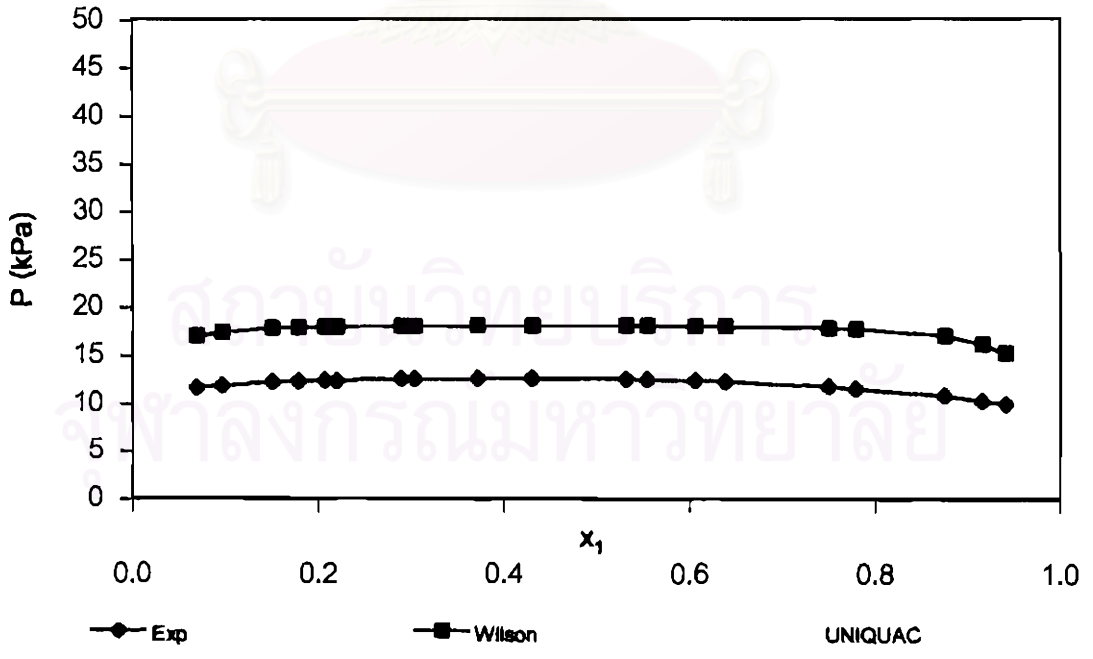

Figure 4.74 P (kPa) of butanenitrile (1) and 2-butanol (2) system at 323.15 K based on parameters from H^E data at 298.15 K.

4.5 Sensitivity

There are two parts in this section as discussed below:

4.5.1 Based on VLE data

The four adjustable parameters were listed in Table 4.2 are used to calculate the sensitivity based on VLE data.

Sensitivity results of thirteen binary systems are reported in Figures 4.75 - 4.87. The percent average absolute deviations, %AAD (P) are less than 13% in all cases.

As the parameters change in the same percent error, the %AAD (P) of the mixtures slightly increases at constant temperature and composition. It can be explained that the interaction binary parameters of two models are slightly sensitive on pressure.

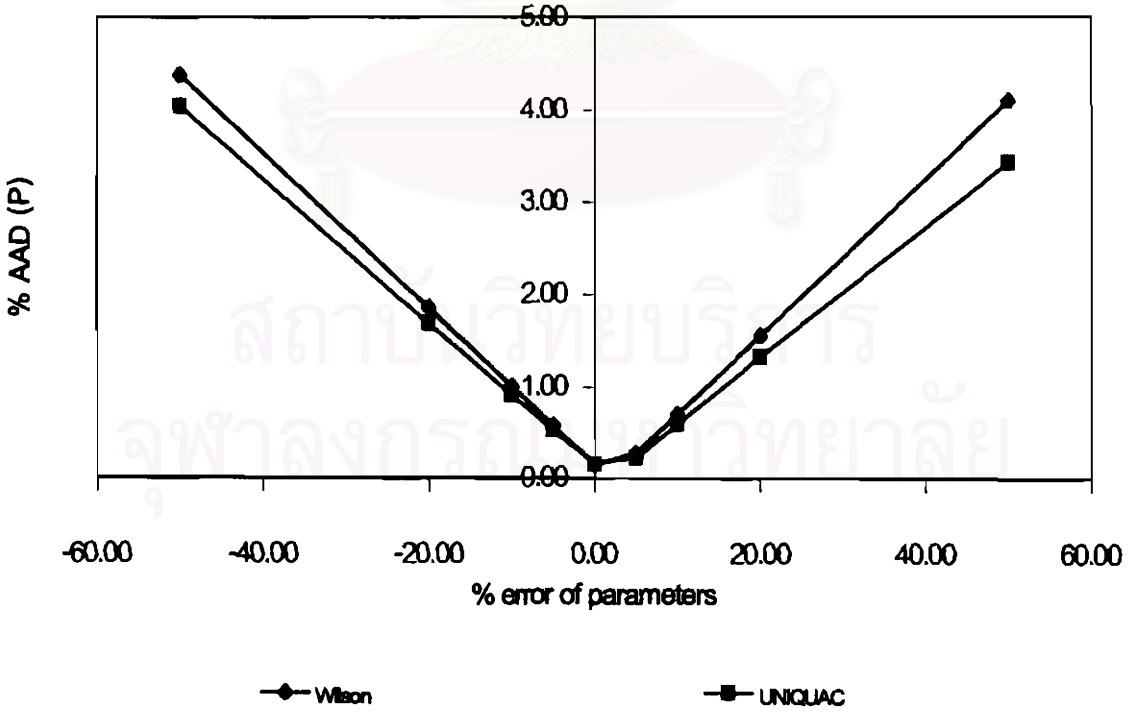

Figure 4.75 Sensitivity of benzene (1) and cyclohexane (2) system at 323.15 K based on VLE data.

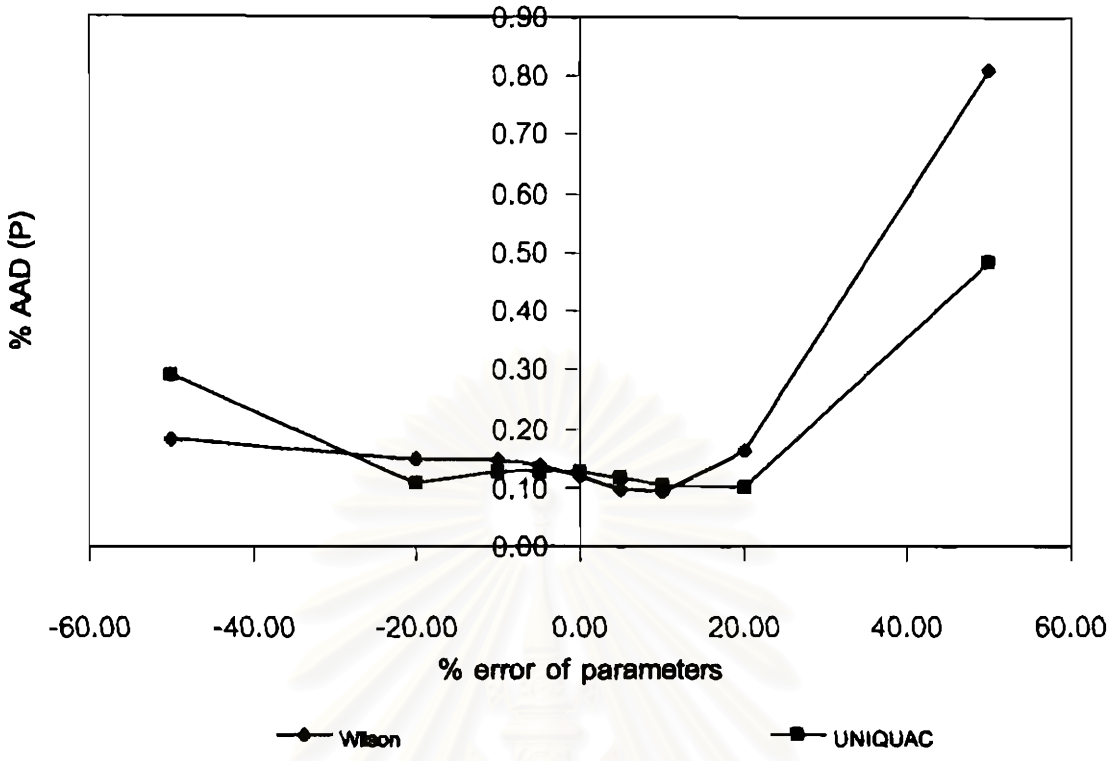

Figure 4.76 Sensitivity of 1-chloropentane (1) and di-n-butyl ether (2) system at 323.15 K based on VLE data.

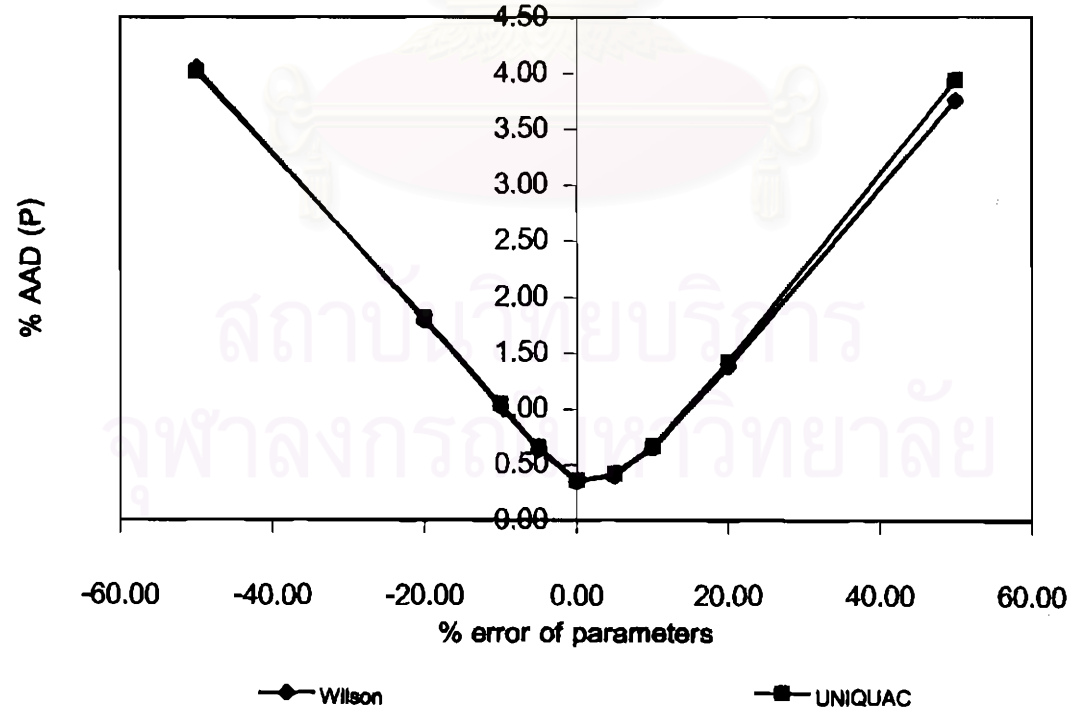

Figure 4.77 Sensitivity of 1,2-dichloroethane (1) and di-n-butyl ether (2) system at 350.00 K based on VLE data.

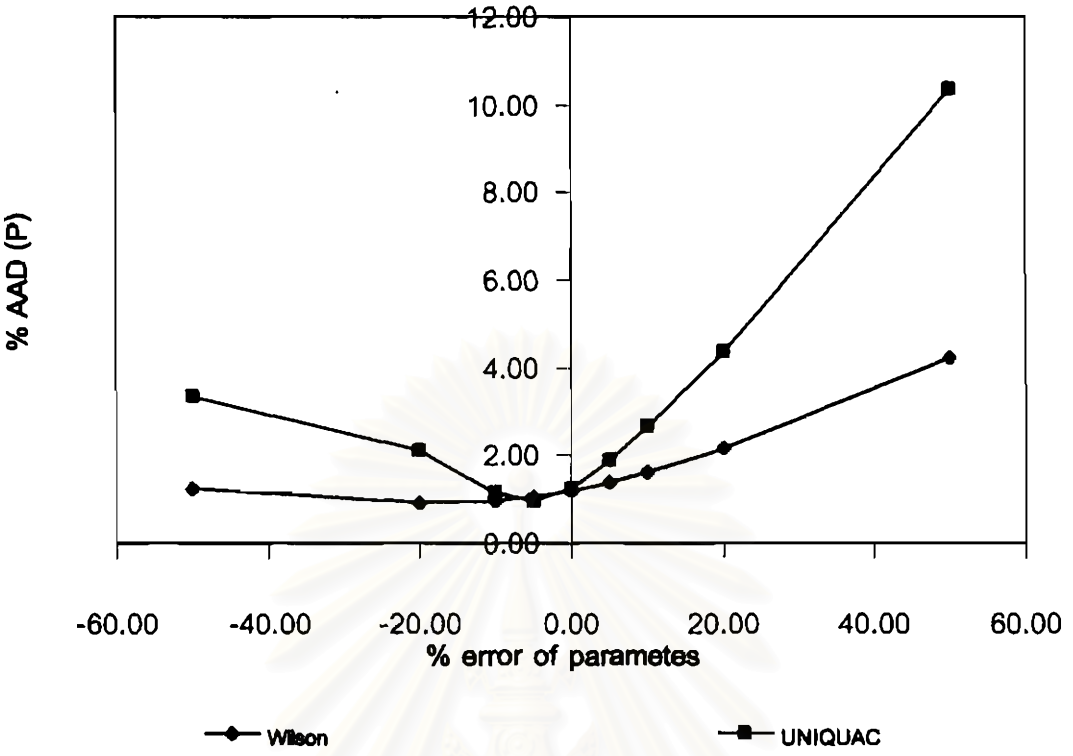

Figure 4.78 Sensitivity of 1,1,1-trichloroethane (1) and di-n-butyl ether (2) system at 343.15 K based on VLE data.

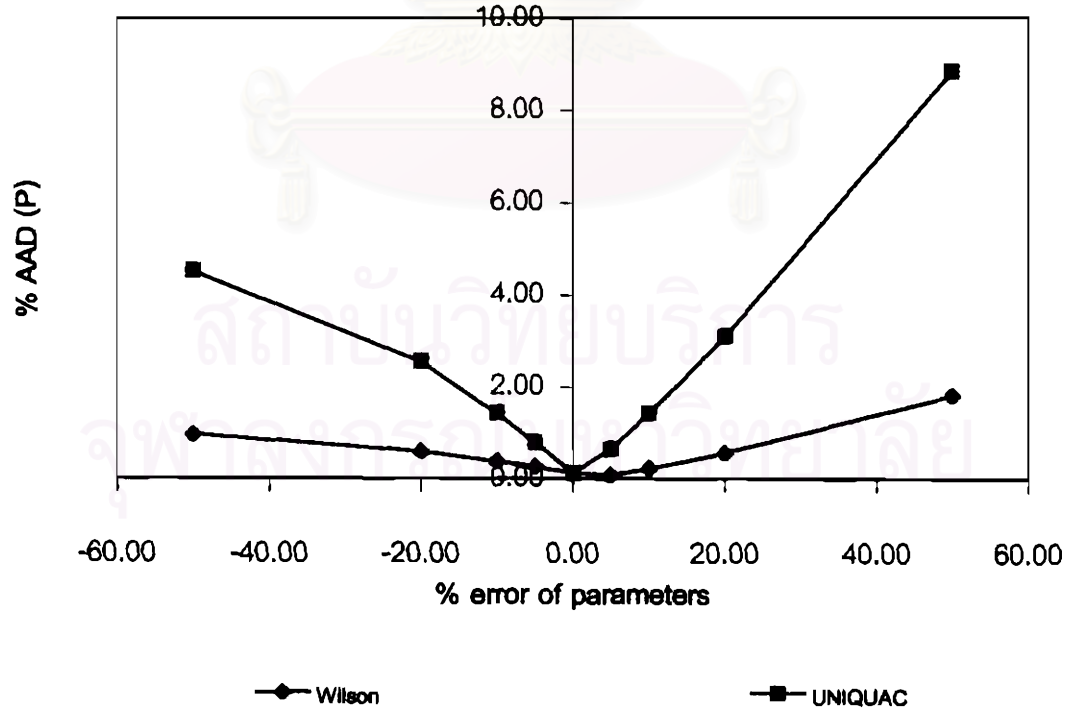

Figure 4.79 Sensitivity of toluene (1) and 1-chlorohexane (2) system at 343.15 K based on VLE data.

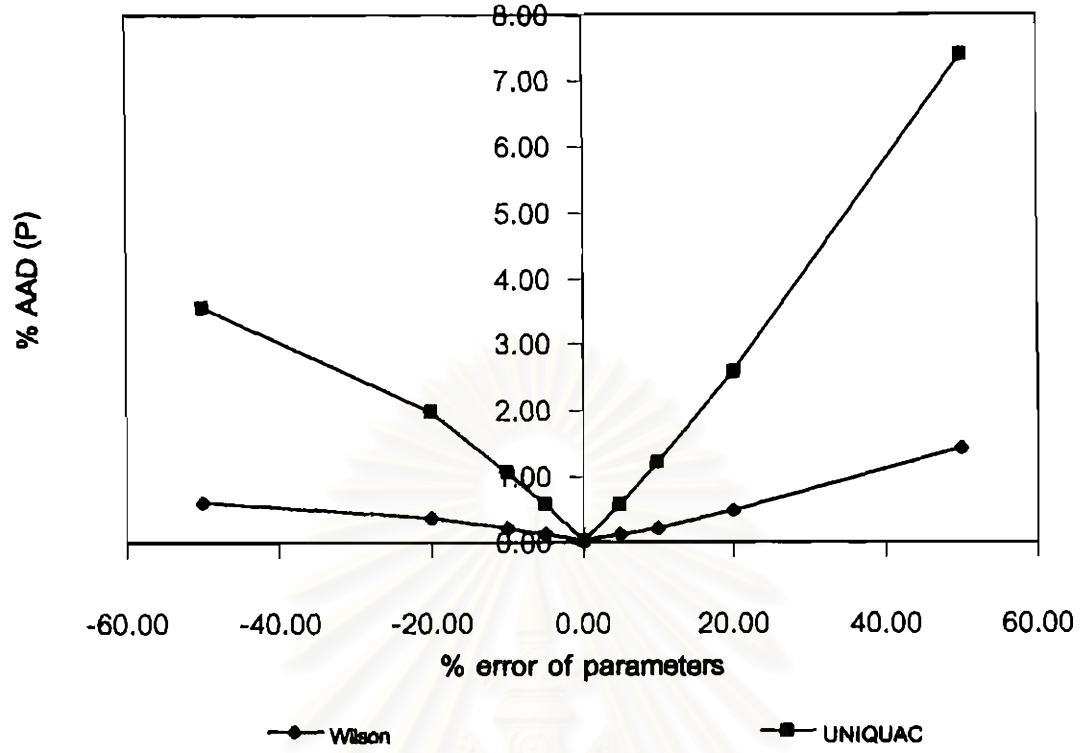

Figure 4.80 Sensitivity of 1-chlorohexane (1) and ethylbenzene (2) system at 343.15 K based on VLE data.

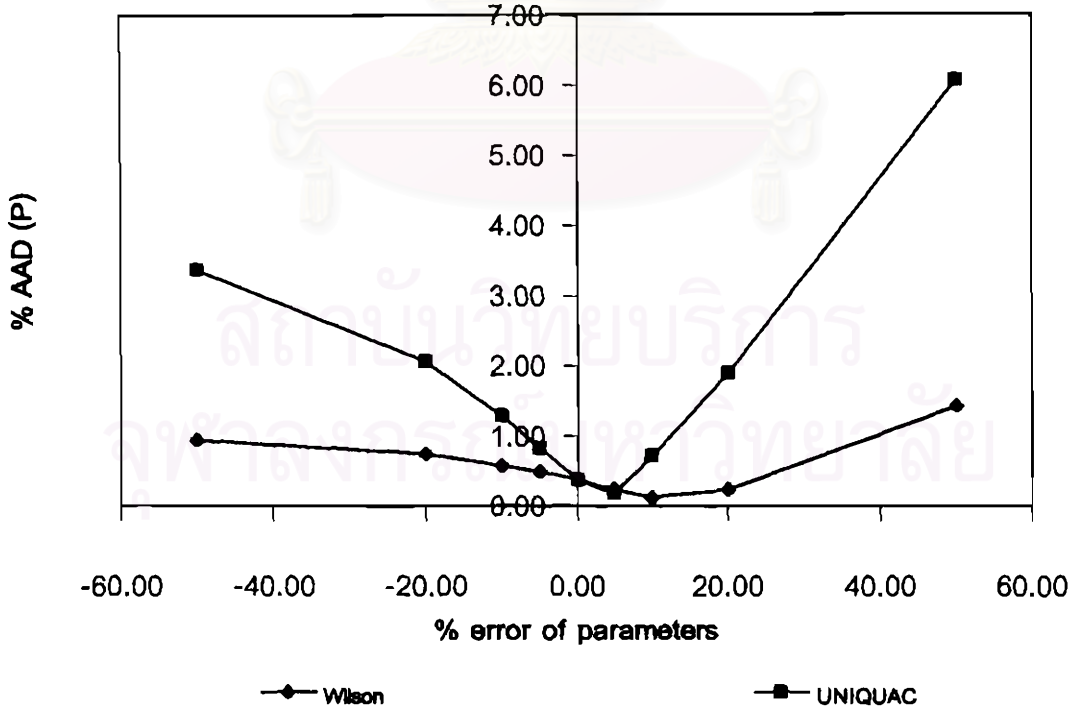

Figure 4.81 Sensitivity of 1-chlorohexane (1) and n-propylbenzene (2) system at 363.15 K based on VLE data.

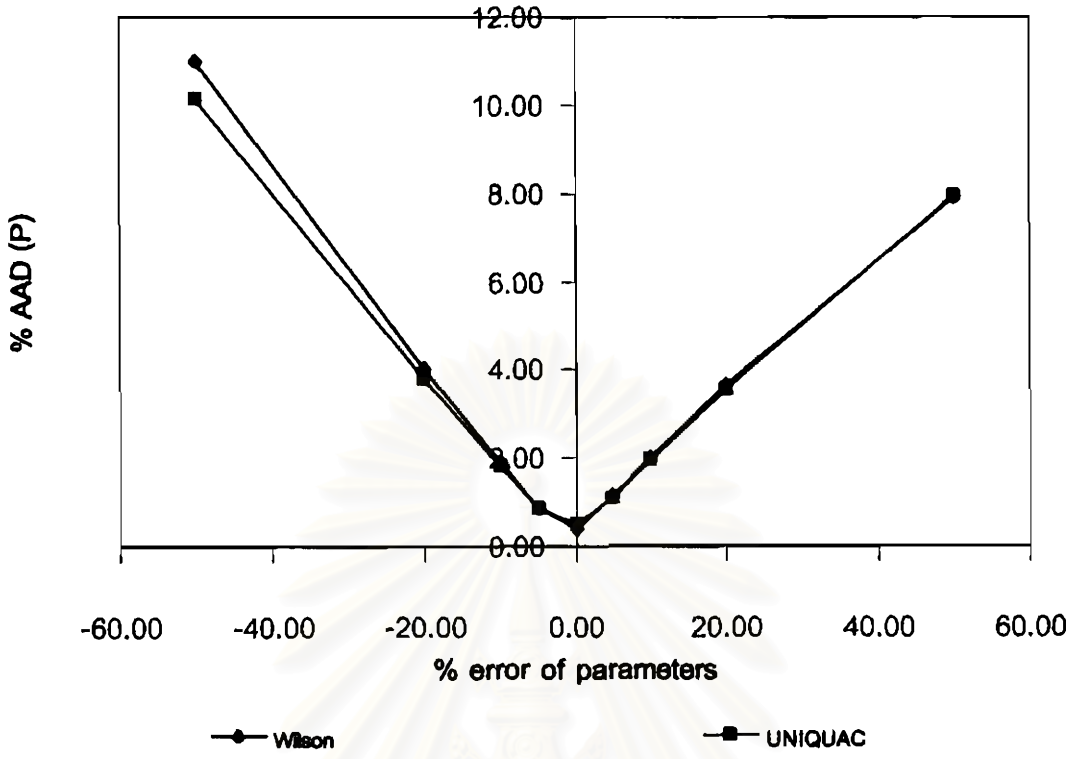

Figure 4.82 Sensitivity of 1,2-epoxybutane (1) and methanol (2) system at 298.15 K based on VLE data.

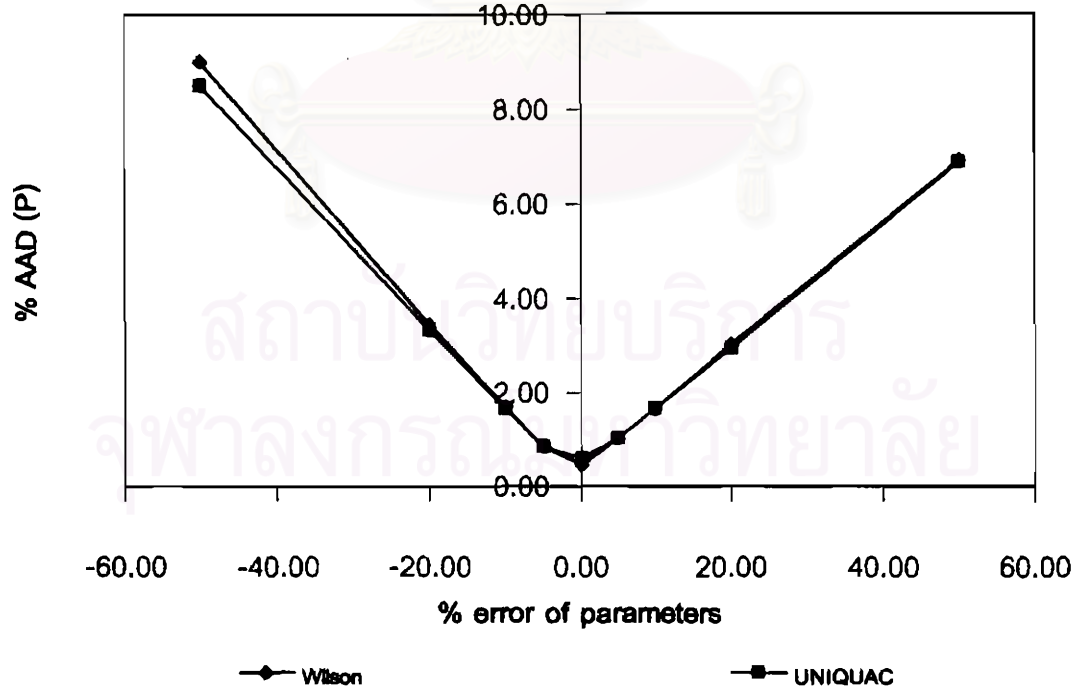

Figure 4.83 Sensitivity of 1,2-epoxybutane (1) and ethanol (2) system at 298.15 K based on VLE data.

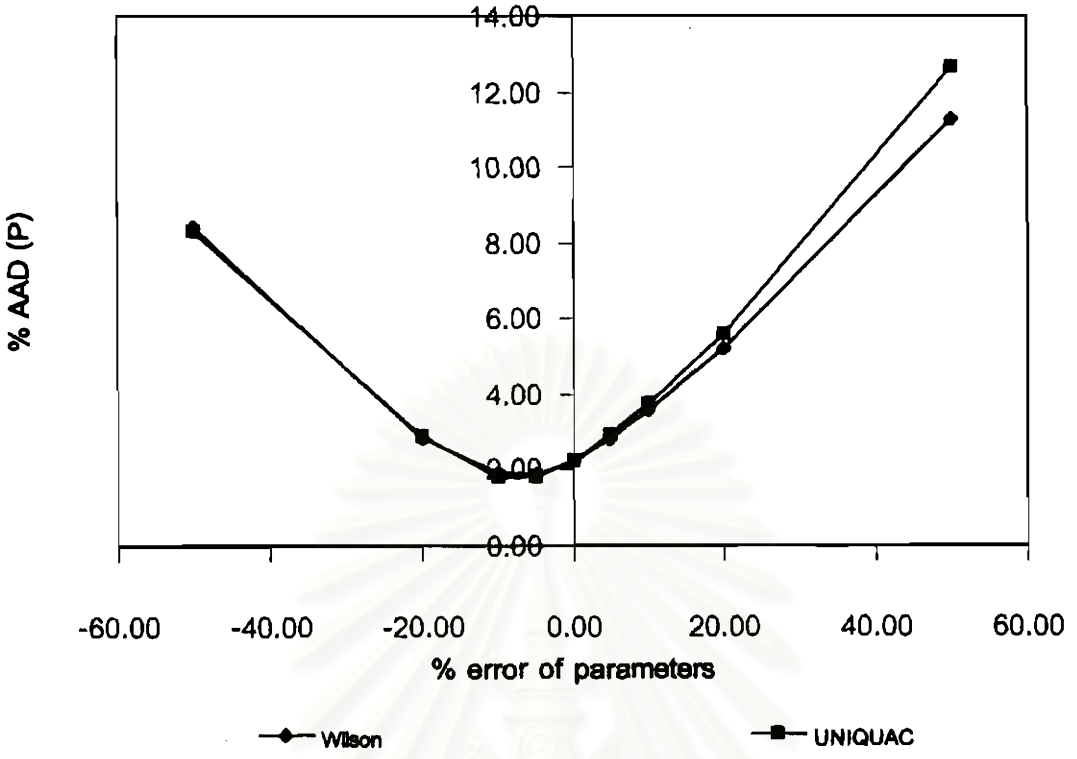

Figure 4.84 Sensitivity of 1,2-epoxybutane (1) and 2-propanol (2) system at 298.15 K based on VLE data.

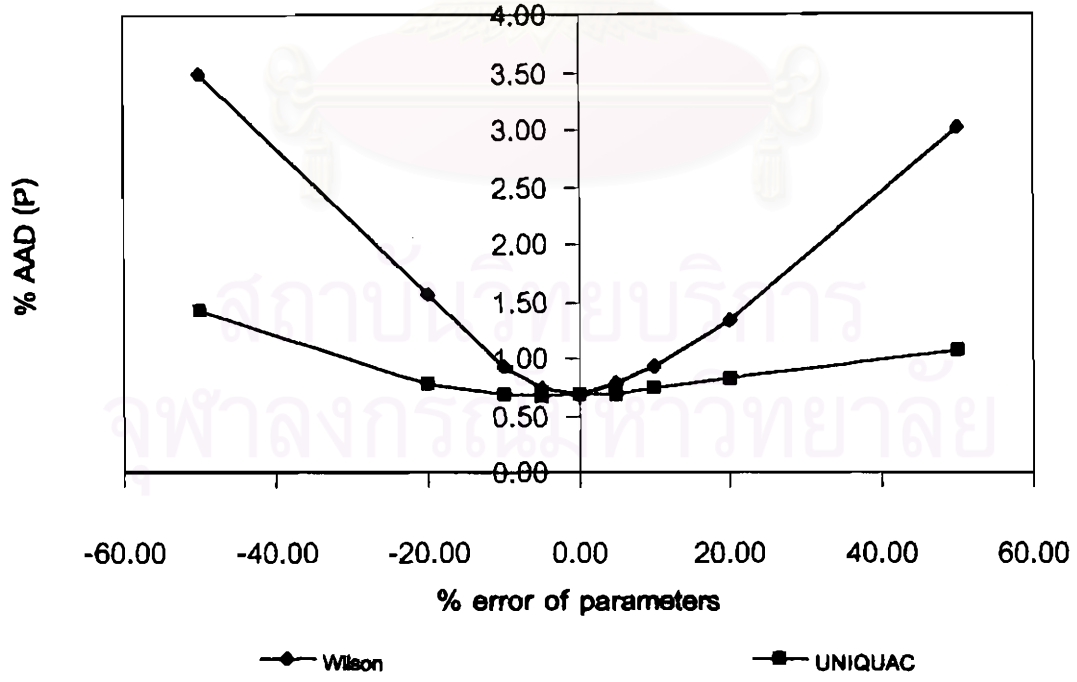

Figure 4.85 Sensitivity of ethyl formate (1) and benzene (2) system at 323.15 K based on VLE data.

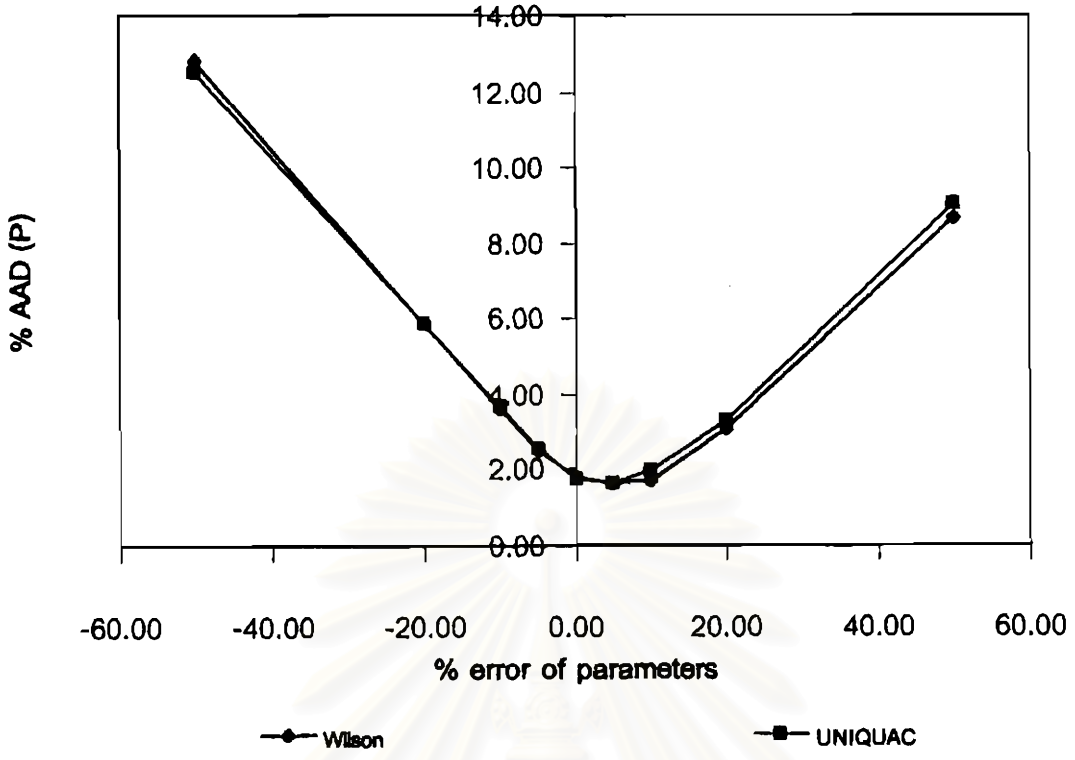

Figure 4.86 Sensitivity of ethyl formate (1) and cyclohexane (2) system at 323.15 K based on VLE data.

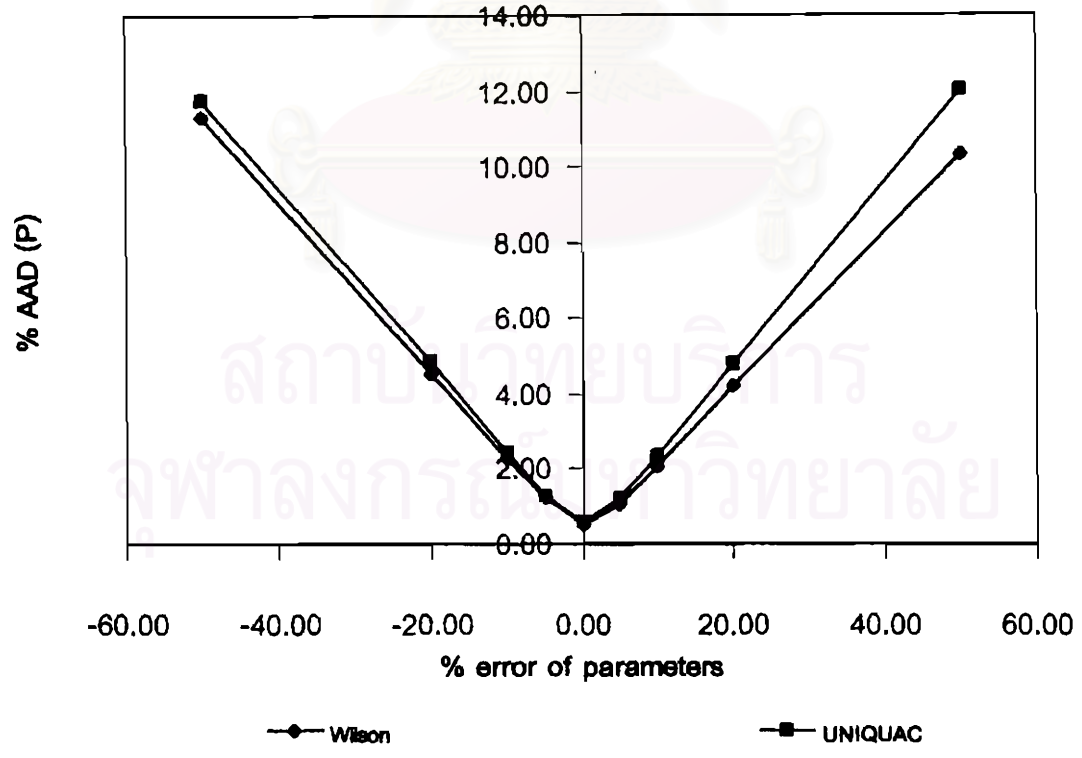

Figure 4.87 Sensitivity of butanenitrile (1) and 2-butanol (2) system at 298.15 K based on VLE data.

4.5.2 Based on H^E data

The parameters, which were listed in Table 4.4, are used to calculate the sensitivity based on H^E data.

Sensitivity results of thirteen binary mixtures at 298.15 K are presented in Figures 4.88 - 4.100. At the parameters' error up to 50%, the highest value of percent average absolute deviations, %AAD (H^E) is 312.74 % for 1,1,1-trichloroethane and di-n-butyl ether system as reported in Table E.6.4 whereas the lowest value of %AAD (H^E) is 9.84% for butanenitrile and 2-butanol system. These values were correlated by UNIQUAC equation.

Moreover, as the parameters change in the increasing percent error, the %AAD (H^E) of the mixtures increases at constant temperature and composition. It can be explained that the interaction binary parameters of two models are sensitive on heat of mixing.

As observed, the UNIQUAC parameters for butanenitrile and 2-butanol system are slightly sensitive on heat of mixing whereas the Wilson parameters of the same system are more sensitive on heat of mixing. For 1,2-epoxybutane + alkanols, ethyl formate + benzene, ethyl formate + cyclohexane systems, the Wilson and UNIQUAC parameters are less sensitive on heat of mixing.

In addition, the %AAD (H^E) is proportional to the absolute error changes in the two model parameters for 1-chlorohexane with three n-alkylbenzenes systems. These behavior can be shown in Figures 4.92 - 4.94.

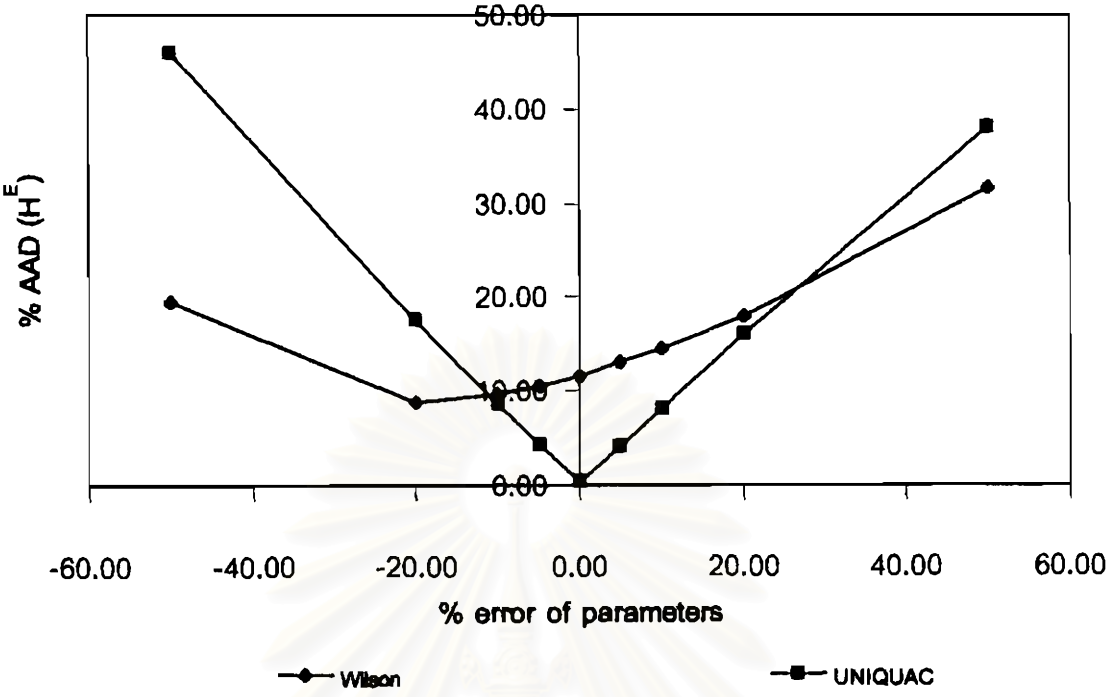

Figure 4.88 Sensitivity of benzene (1) and cyclohexane (2) system at 298.15 K based on H^E data (Meyer et al., 1977).

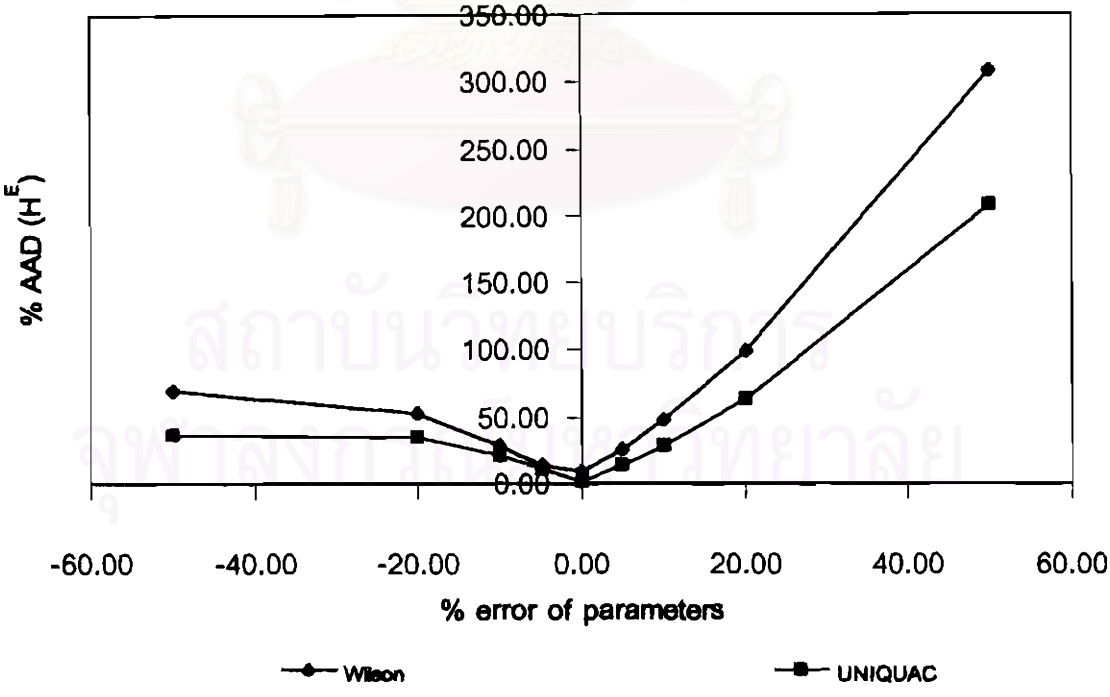

Figure 4.89 Sensitivity of 1-chloropentane (1) and di-n-butyl ether (2) system at 298.15 K based on H^E data.

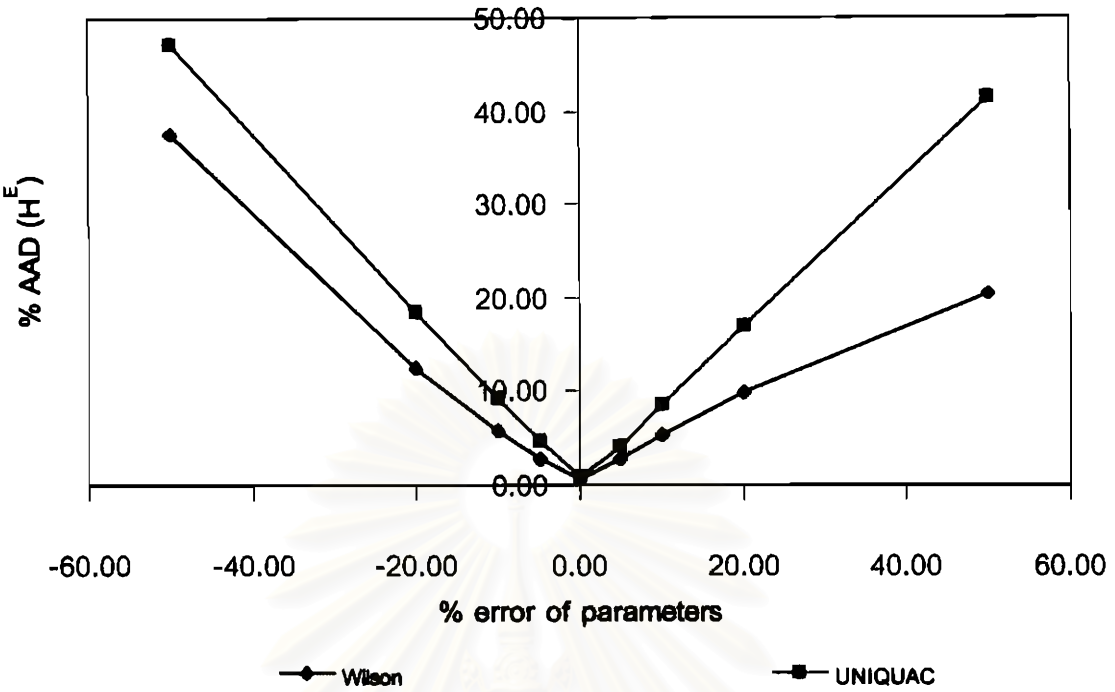

Figure 4.90 Sensitivity of 1,2-dichloroethane (1) and di-n-butyl ether (2) system at 298.15 K based on H^E data.

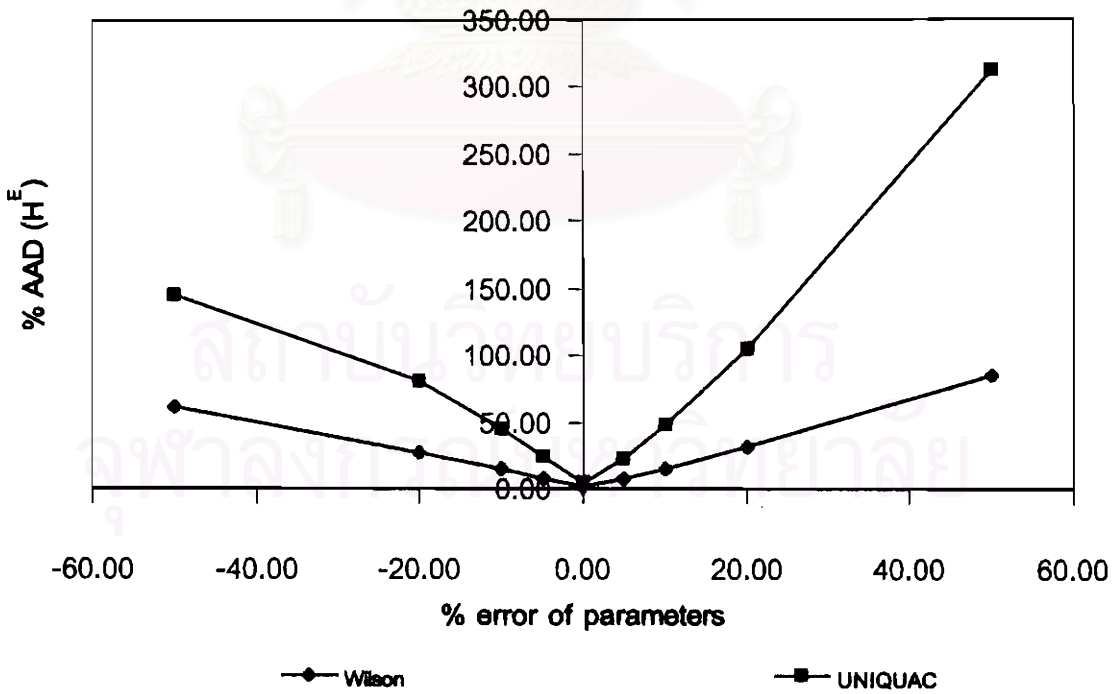

Figure 4.91 Sensitivity of 1,1,1-trichloroethane (1) and di-n-butyl ether (2) system at 298.15 K based on H^E data.

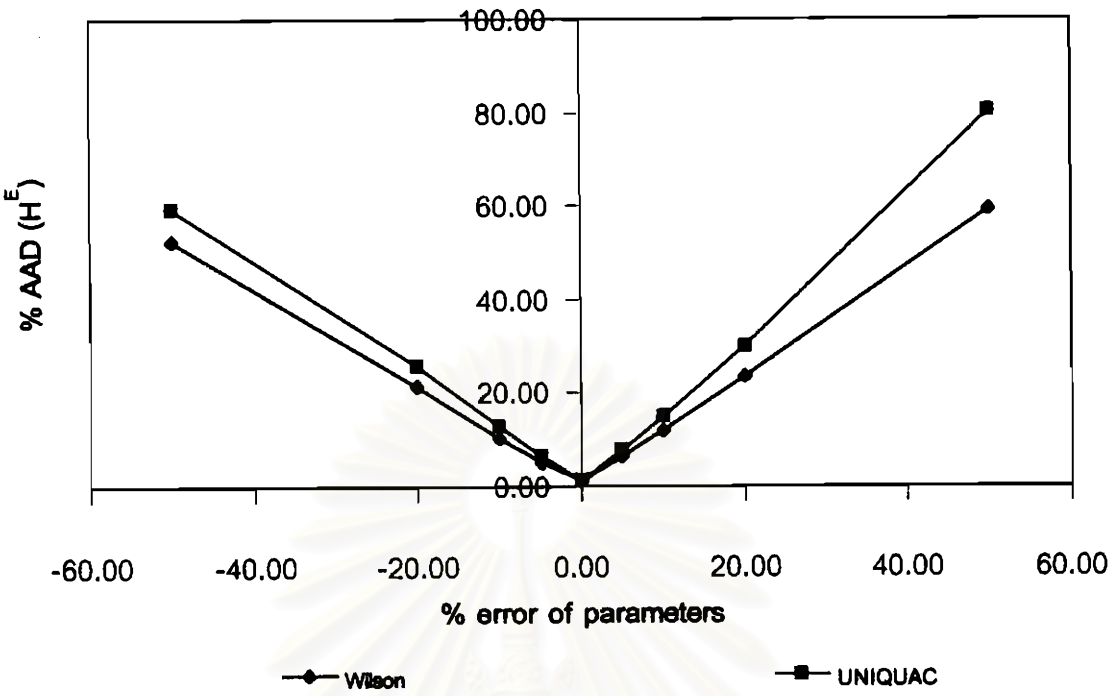

Figure 4.92 Sensitivity of toluene (1) and 1-chlorohexane (2) system at 298.15 K based on H^E data.

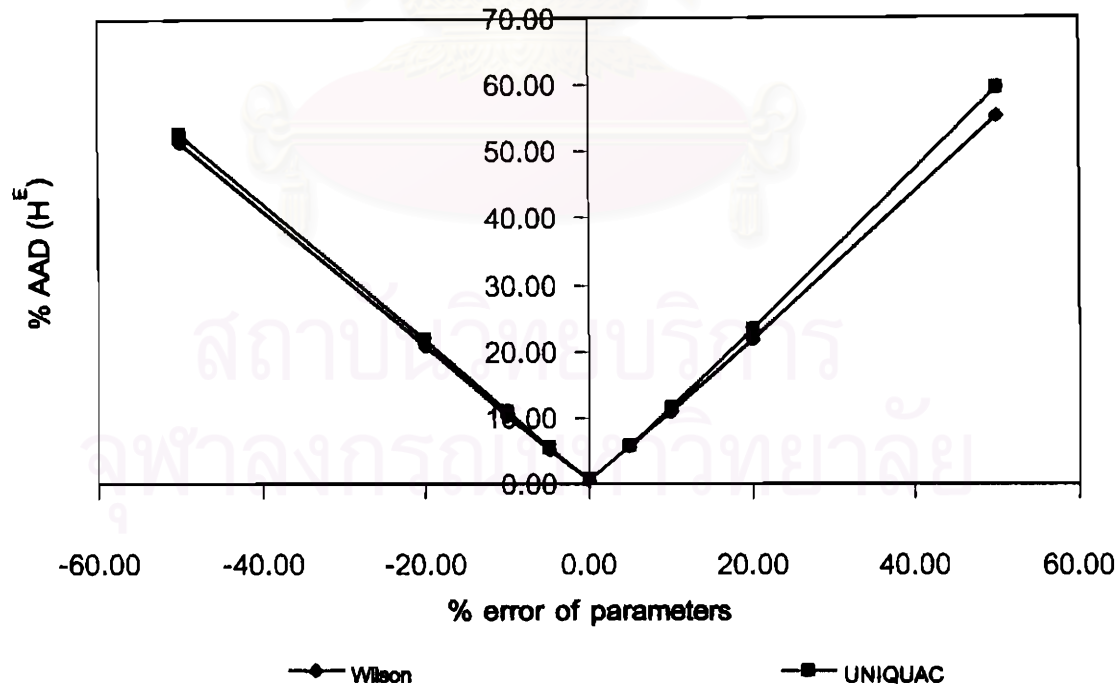

Figure 4.93 Sensitivity of 1-chlorohexane (1) and ethylbenzene (2) system at 298.15 K based on H^E data.

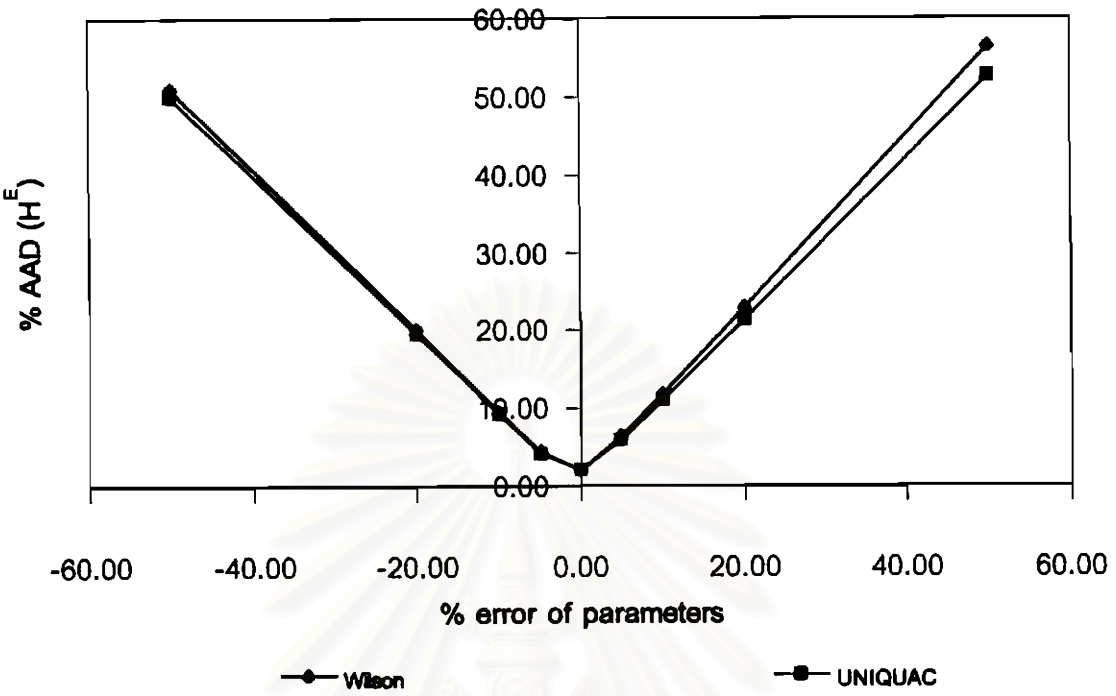

Figure 4.94 Sensitivity of 1-chlorohexane (1) and n-propylbenzene (2) system at 298.15 K based on H^E data.

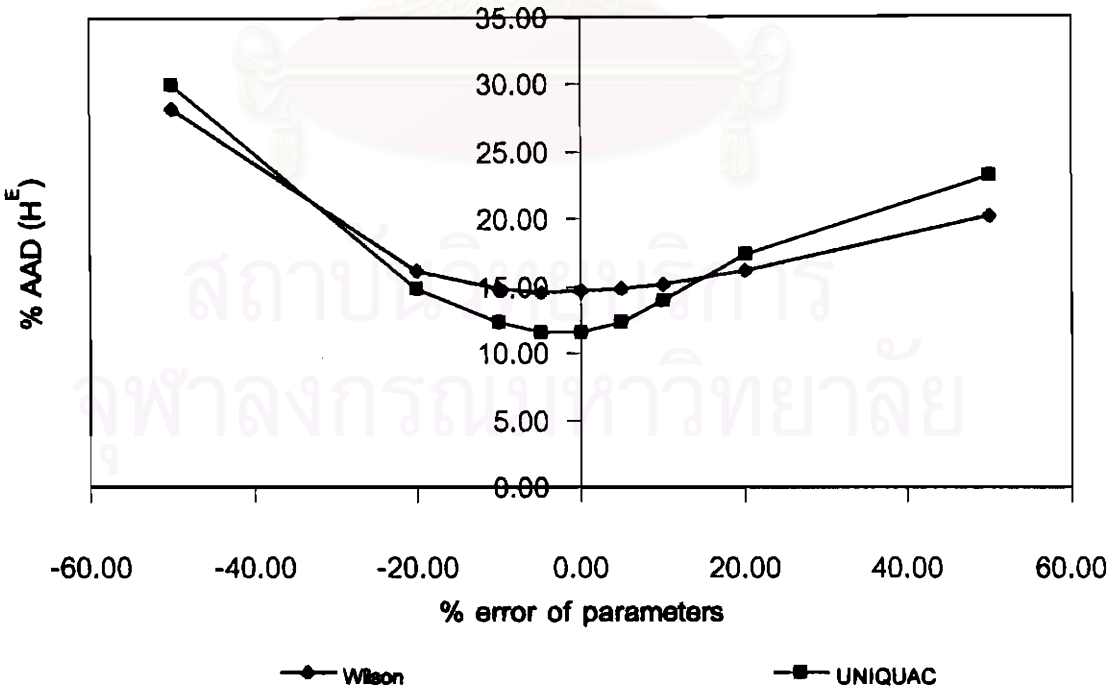

Figure 4.95 Sensitivity of 1,2-epoxybutane (1) and methanol (2) system at 298.15 K based on H^E data.

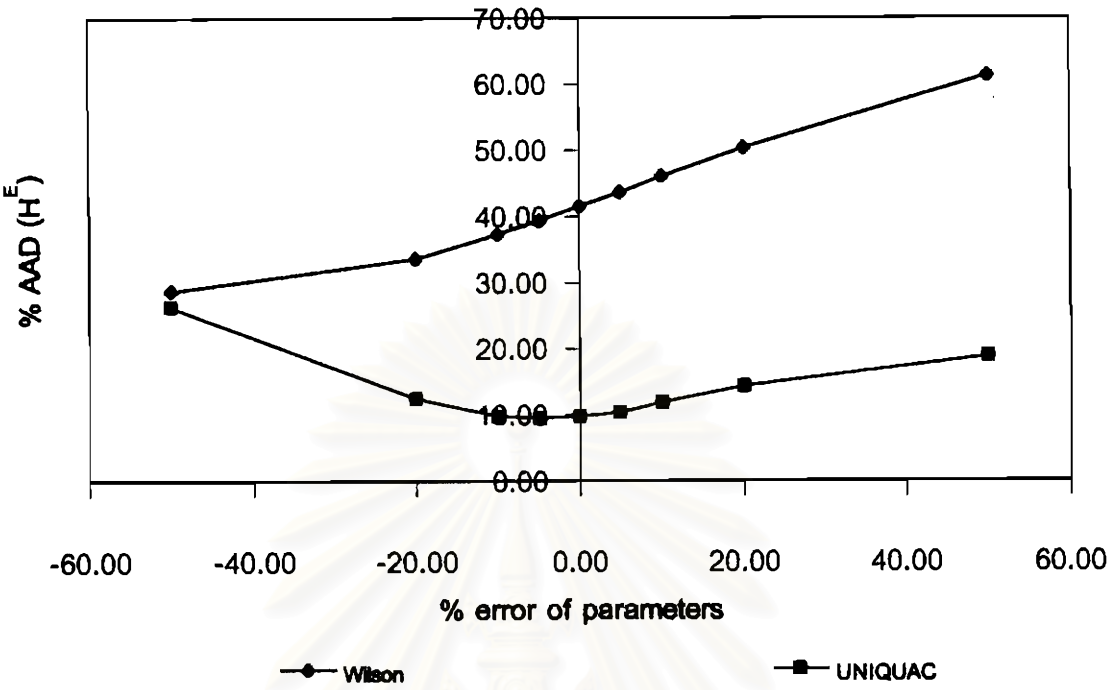

Figure 4.96 Sensitivity of 1,2-epoxybutane (1) and ethanol (2) system at 298.15 K based on H^E data.

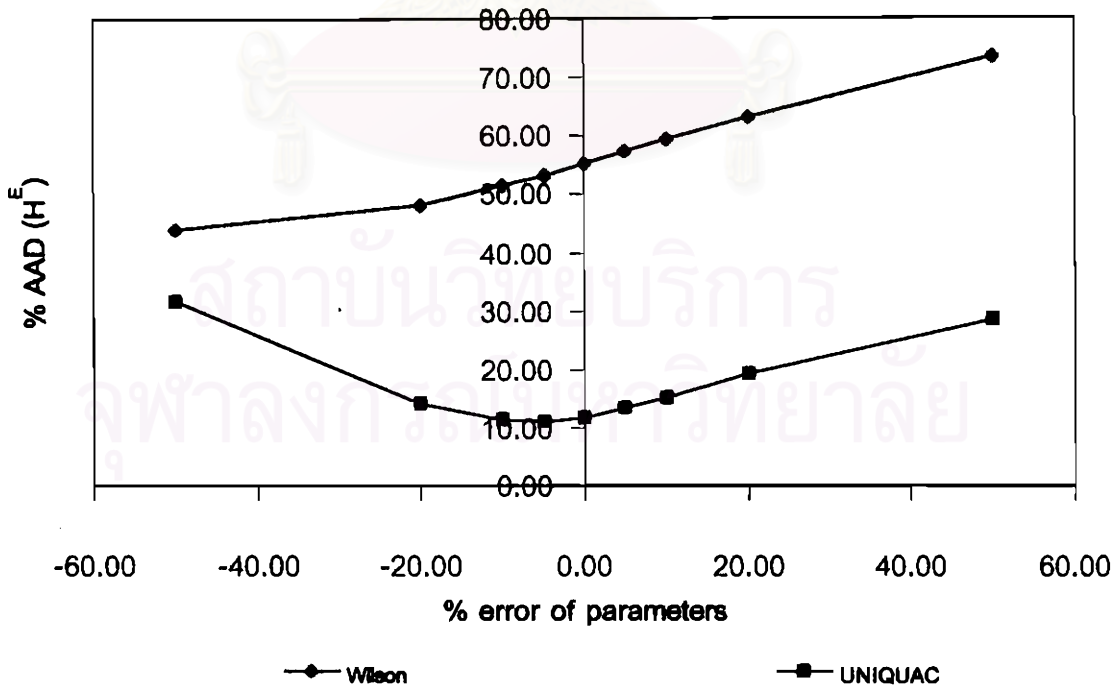

Figure 4.97 Sensitivity of 1,2-epoxybutane (1) and 2-propanol (2) system at 298.15 K based on H^E data.

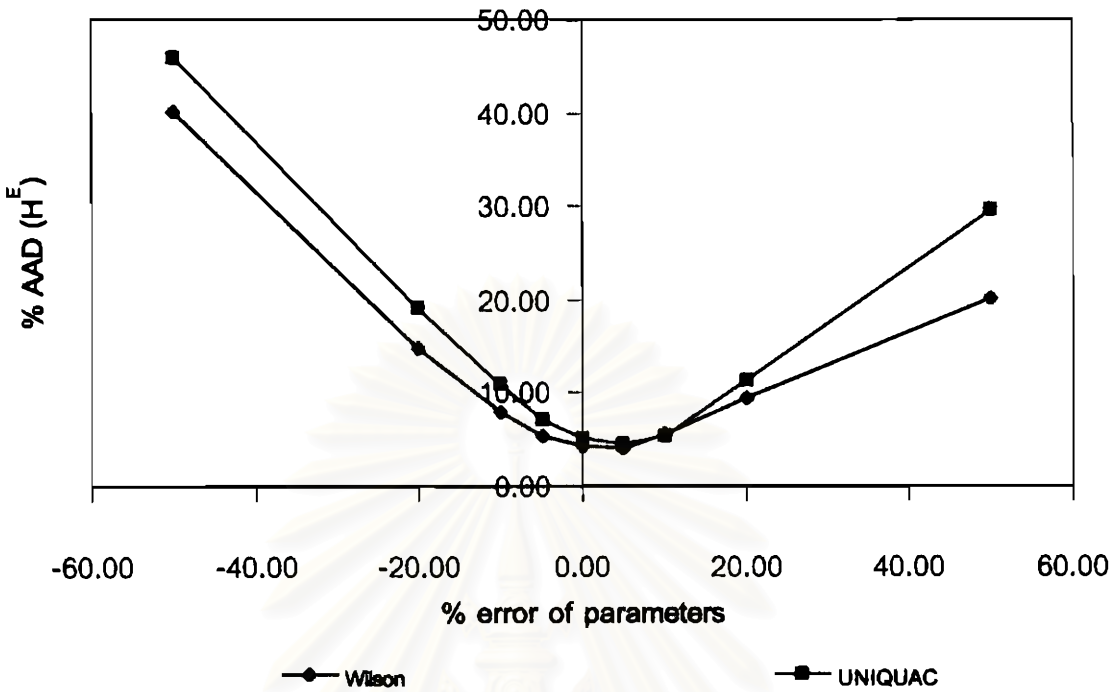

Figure 4.98 Sensitivity of ethyl formate (1) and benzene (2) system at 298.15 K based on H^E data.

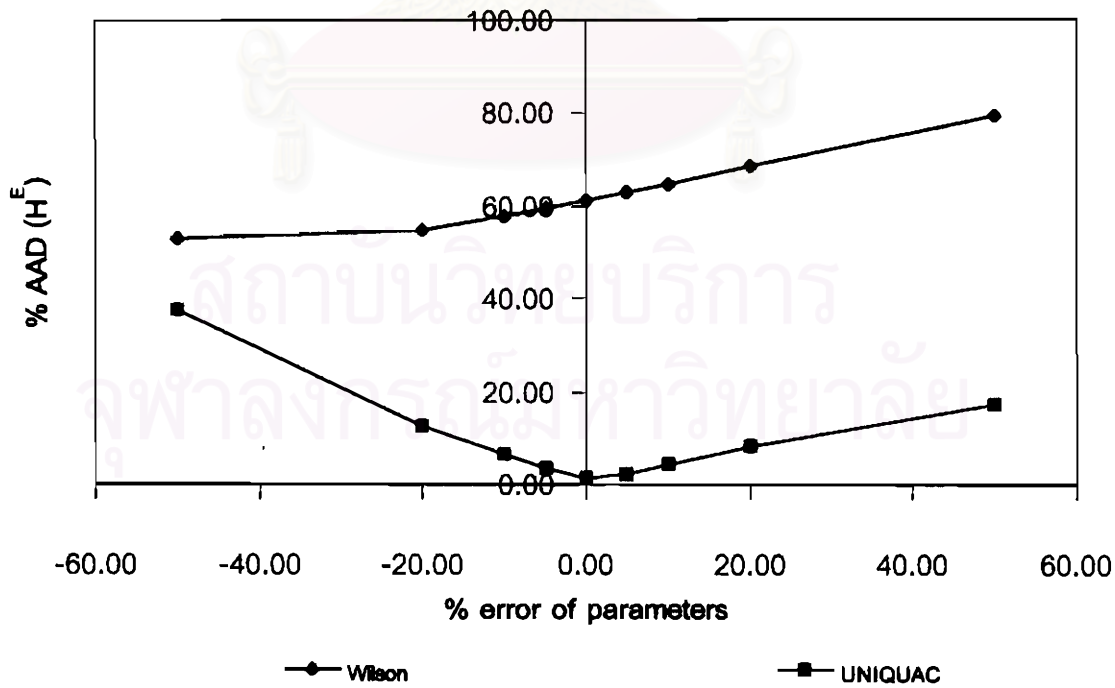

Figure 4.99 Sensitivity of ethyl formate (1) and cyclohexane (2) system at 298.15 K based on H^E data.

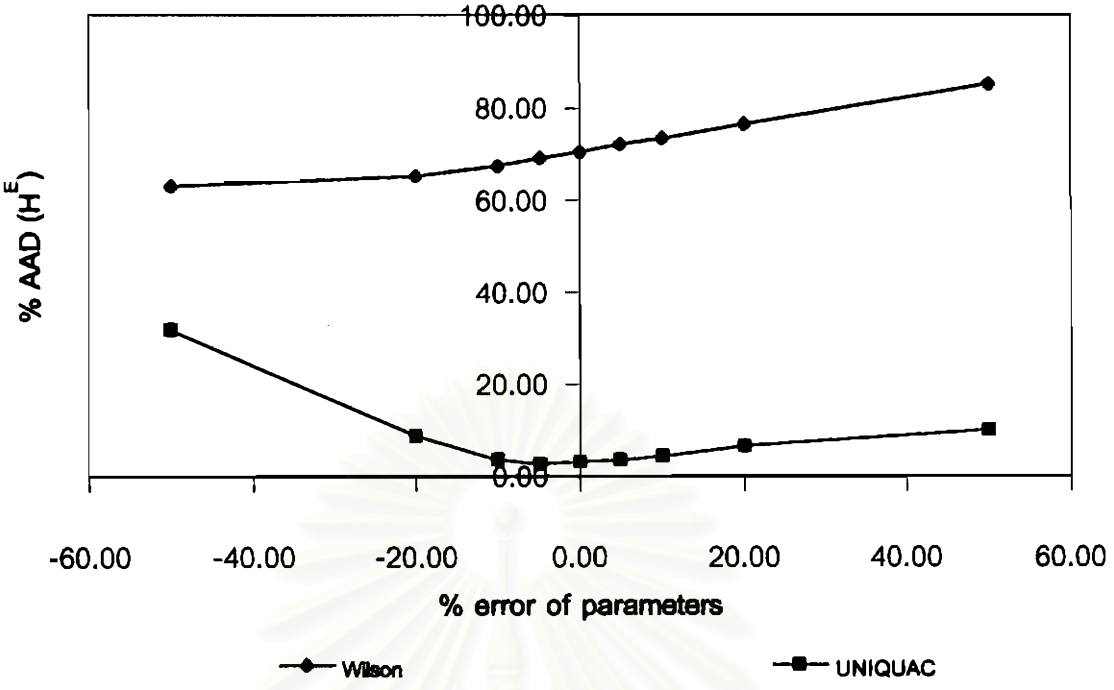

Figure 4.100 Sensitivity of butanenitrile (1) and 2-butanol (2) system at 298.15 K based on H^E data.

4.6 Classification

According to the Ewell classification (Table A.3) constituents in the binary mixtures studied in this thesis belong to four groups of molecules.

First, methanol, ethanol, 2-propanol, 2-butanol and butanenitrile belong to the group II. Second, ethyl formate, di-n-butyl ether and 1,2-epoxybutane are members of the group III. Third, 1,2-dichloroethane and 1,1,1-trichloroethane are a set in the group IV. Finally, benzene, cyclohexane, toluene, ethylbenzene, n-propylbenzene, 1-chloropentane and 1-chlorohexane are a collection in the group V.

Based on H^E data, prediction of H^E by using UNIQUAC equation as shown in Table 4.4 is better than the Wilson equation for mixtures of constituents belong to the groups II + II, II + III, III + V, and V + V but worse for the class III + IV.

Based on VLE data, both the Wilson equation and UNIQUAC equation predict saturation pressure satisfactorily with % AAD of less 2.26 for all systems tested.