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2 성분 액체 용액계의 혼합열

(1,2-dichloroethane-n-heptane, 1,2-dichloroethane-n-butanol, n-heptane-n-butanol)

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Heats of Mixing for the Binary Liquid Mixtures

(1,2-dichloroethane-n-heptane, 1,2-dichloroethane-n-butanol, n-heptane-n-butanol)

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요 약

1,2-dichloroethane-n-heptane, 1,2-dichloroethane-n-butanol 系와 n-heptane-n-butanol 系의 混合熱을 15°C, 25°C, 35°C 와 45°C 에서 測定하였으며 이로부터 partial heats of mixing 값들을 구한 후 같은 溫度에서 過剩熱力學的 性質을 計算하였고 partial excess Gibbs free energy 를 利用하여 等溫氣液平衡值를 推算하였으며, 이 값을 混合熱로부터 計算된 過剩 Gibbs free energy 와 함께 total pressure 法으로 計算된 35°C 와 45°C 에서의 값들과 比較하여 보았고 더욱 150 mmHg 와 300mmHg 에서 等壓氣液平衡值를 推算하였다.

Abstract

Heats of mixing for the 1,2-dichloroethane-n-heptane, 1,2-dichloroethane-n-butanol and n-heptane-n-butanol systems were measured at 15°C, 25°C, 35°C and 45°C. From the heats of mixing, partial heats of mixing were calculated, and then excess thermodynamic properties for each binary solutions were calculated. Using the partial excess Gibbs free energy, the values of isothermal vapor-liquid equilibrium were estimated. The calculated excess Gibbs free energy and isothermal vapor-liquid equilibrium data from heats of mixing were compared with those by total pressure method at 35°C and 45°C. Furthermore, the isobaric vapor-liquid equilibrium data were estimated at 150mmHg and 300mmHg.

1. 序 論

蒸溜 또는 抽出等 分離裝置의 設計 및 運轉에 있어서는 液體 溶液系의 氣-液平衡 및 液-液平衡데이터가 必要하게 되는데 이들 데이터는 液體 溶液系의 過剩熱力學的 性質과 密接한 關係가 있다.

이와같은 液體 溶液系의 過剩熱力學的 性質을 理論的으로 解析함에 있어서 가장 重要視되는 點은 液體混合物의 分子거동 및 分布에서 오는¹⁾ 液相에서의 非理想性으로서 이와같은 非理想性에 의한 영향이 가장 顯著한 것으로는 混合熱을 들 수 있다.

本 研究에서는 1,2-dichloroethane-n-heptane 系, 1,2-dichloroethane-n-butanol 系와 n-heptane-n-butanol 系의 混合熱을 15°C, 25°C, 35°C 와 45°C에서 各 組成에 對하여 測定하였으며 이로부터 過剩熱力學的 特性值를 溫度 및 組成에 對한 一般化된 關係式으로 表示하였다²⁾. 더욱이로부터 等溫氣液平衡值³⁾⁴⁾⁵⁾ 및 等壓氣液平衡值의 推算을 試圖하였다.

2. 實驗裝置 및 方法

2-1 實驗裝置

混合熱을 測定하는데는 現在까지 많은 熱量計가 개발되어 왔으며⁶⁾ 本 研究에서는 mixing cell 內의 氣相除去, 混合에 따르는 蒸氣凝縮現象 및 부피變化를 考慮하여 一定한 壓力下에서 混合이 이루어지도록 함으로써 그 正確성이 相當히 높여진 Larkin-McGlashan 熱量計⁷⁾를 製作하여 使用하였다.

熱量計는 測定部分과 mixing jacket 두 部分으로 構成되어 있으며, mixing jacket 內에 裝填된 mixing cell 은 硝子製로써 직경 2.5cm 높이 6cm 인 원통형이고 약 18.7 Ω의 加熱用 coil 을 使用하였다. 또한 溫度變化를 測定하기 위하여 200Ω의 thermister 를 使用하였으며, 測定部分은 Wheatstone bridge 회로가 中心이고, 이를 recorder 에 연결하였으며 加熱用 coil 의 전원으

로는 直流전원을 使用하였고 1.03 volt 의 水銀전지를 Wheatstone bridge 의 표준전지로 使用하였다.

2-2 實驗 方法

mixing cell 內에 잘 精製된 水銀을 채우고 完全히 脫氣시킨 試料를 正確히 秤量하여 各 各 分離주입한 후 mixing jacket 內에 裝填한다. mixing jacket 을 一定溫度로 유지된 '항온조(±0.05°C) 속에서 4~5時間 방치한 다음 mixing cell 內의 試料와 항온조간에 熱平衡이 이루어진 것을 확인한 후 mixing cell 과 주위와를 斷熱시키기 위하여 mixing jacket 內를 10~15 mmHg 로 감압시킨다. 다음에 mixing jacket 을 180~270°로 서서히 회전시켜 試料가 完全 混合되도록하여 溫度變化를 測定한다. 다음 加熱用 coil 에 100 sec 동안 직류전류(약 3volt, 0.15ampere)를 通하여 이때의 溫度變化를 測定하여 液體混合物의 熱容量을 얻고 混合時의 溫度變化로부터 混合熱을 計算한다.

3. 實驗 結果

1,2-dichloroethane(1)-n-heptane(2)系 1,2-dichloroethane(1)-n-butanol(2)系와 n-heptane(1)-n-butanol (2)系의 混合熱을 15°C, 25°C, 35°C 와 45°C에서 測定하였으며 (Table 1), 測定된 混合熱데이터는 一定溫度에서

$$\Delta H^E/X_1X_2 = a + bX_1 + cX_1^2 + dX_1^3 + eX_1^4 \quad (1)$$
의 多項式으로 表되었다. 여기서 常數 a, b, c, d, e 를 各 溫度에 對하여 計算하였고 (Table 2) 測定한 값과 (1)式으로 計算된 값을 plot 하면 Fig. 1 과 같다.

3-1 過剩 熱力學的 特性值

一定 組成下에서 混合溶液의 熱容量을 溫度의 函數로 表示하면 다음과 같다⁸⁾.

$$\Delta C_p/X_1X_2R = A + BT + CT^2 \quad (\text{一定組成下}) \quad (2)$$
熱力學的 特性值는 윗식과의 관련하에

$$\Delta H^E/X_1X_2R = AT + BT^2/2 + CT^3/3 + D \quad (3)$$

Table 1. Heats of Mixing for the 1,2-Dichloroethane(1)-n-Heptane System

$\Delta H^E(\text{cal/g-mole})$				
X_1	15°C	25°C	35°C	45°C
0.0765	113.3	133.1	156.8	189.2
0.1386	192.2	224.0	256.7	303.7
0.2795	334.6	368.7	411.5	467.3
0.3620	381.4	415.3	460.0	511.6
0.4408	405.3	436.6	479.6	524.5
0.5187	409.0	438.4	477.0	515.9
0.5995	396.5	422.9	456.7	492.4
0.6819	365.0	390.5	422.5	460.1
0.7683	306.7	336.5	372.9	414.7
0.9296	124.9	147.4	185.2	224.5

Heats of Mixing for the 1,2-Dichloroethane(1)-n-Butanol(2) System

$\Delta H^E(\text{cal/g-mole})$				
X_1	15°C	25°C	35°C	45°C
0.1886	148.4	173.4	211.4	250.2
0.2764	220.7	250.7	285.1	335.9
0.3492	267.1	307.8	355.1	396.4
0.4219	307.6	357.1	402.5	438.1
0.5028	360.1	405.2	441.3	476.4
0.5993	395.3	434.8	465.3	496.5
0.6998	392.0	430.7	455.2	489.1
0.7897	356.7	390.2	423.1	462.2
0.8426	327.8	352.4	391.9	429.1
0.9197	242.2	273.1	308.9	240.3

Heats of Mixing for the n-Heptane(1)-n-Butanol(2) System

$\Delta H^E(\text{cal/g-mole})$				
X_1	15°C	25°C	35°C	45°C
0.0911	22.4	30.0	38.5	45.8
0.1837	45.0	59.2	75.8	92.4
0.2701	63.3	86.4	107.5	133.9
0.3592	82.5	109.7	136.5	171.0
0.4520	96.1	128.1	159.5	197.6
0.5412	105.9	140.8	173.7	216.1
0.6290	109.0	145.9	182.3	222.3
0.7214	108.8	142.3	180.1	220.5
0.8293	91.6	124.8	160.3	197.4
0.9125	70.3	98.1	129.8	159.8

Table 2. Constants of Equation(1) for the 1,2-Dichloroethane-n-Heptane System

	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>
15°C	1542.08	870.36	-2225.68	1734.57	117.23
25°C	1881.77	139.98	-1463.31	799.50	1155.14
35°C	2344.16	-2022.48	5937.92	-11570.15	8743.21
45°C	2900.61	-3460.30	8278.14	-15177.73	11764.75

Constants of Equation(1) for the 1,2-Dichloroethane-n-Butanol System

	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>
15°C	1807.02	-10112.56	40877.96	-60246.96	32210.12
25°C	2383.78	-14768.79	58431.05	-86574.91	45829.82
35°C	2866.71	-17224.71	66884.56	-100437.62	54079.45
45°C	3088.68	-16395.30	62698.37	-95946.56	52822.47

Constants of Equation(1) for the n-Heptane(1)-n-Butanol (2) System

	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>
15°C	307.73	-737.71	4913.56	-8800.04	5526.79
25°C	424.47	-1232.27	7890.43	-14357.60	9023.88
35°C	563.83	-1827.59	10901.37	-19800.20	12518.96
45°C	643.51	-1854.28	12617.92	-23908.95	15419.76

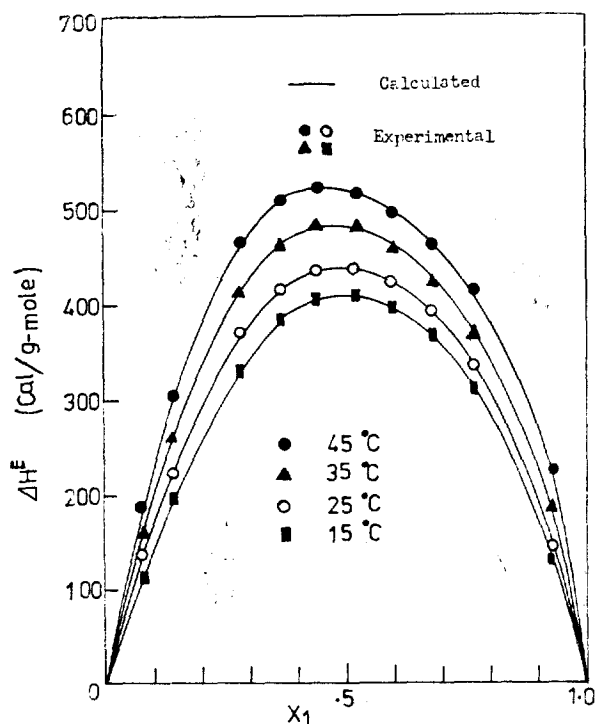


Fig. 1a. Experimental Heat of Mixing for the 1,2-Dichloroethane(1)-n-Heptane(2) System

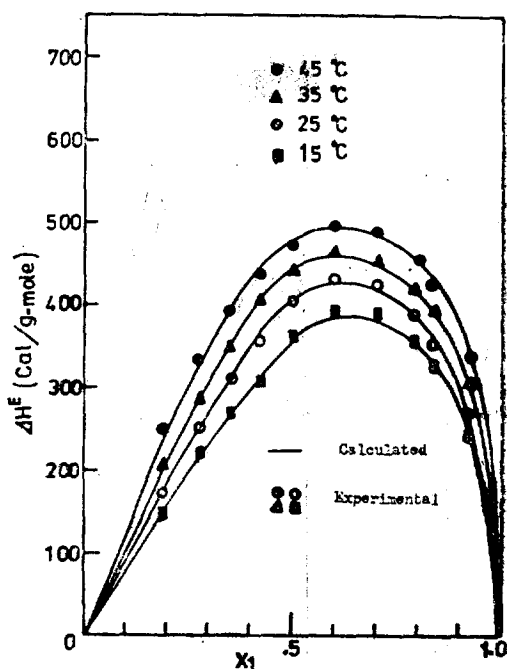


Fig. 1b. Experimental Heat of Mixing for the 1,2-Dichloroethane(1)-n-Butanol(2) System

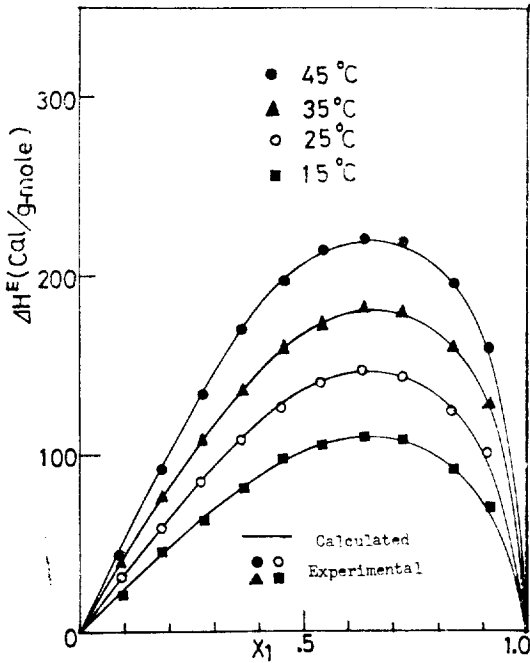


Fig. 1c. Experimental Heat of Mixing for the n-Heptane(1)-n-Butanol(2) System

$$\Delta G^E/X_1X_2R = -AT\ln T - BT^2/2 - CT^3/6 + D + IT \quad (4)$$

$$\Delta S^E/X_1X_2R = A\ln T + BT + CT^2/2 + (A - I) \quad (5)$$

가 되며 partial molar property 는

$$\overline{\Delta H}_i^E/R = A_iT + B_iT^2/2 + C_iT^3/3 + D_i \quad (6)$$

$$\overline{\Delta G}_i^E/R = -A_iT\ln T - B_iT^2/2 - C_iT^3/6 + D_i + I_iT \quad (7)$$

$$\overline{\Delta S}_i^E/R = A_i\ln T + B_iT + C_iT^2/2 + (A_i - I_i) \quad (8)$$

이다. (2), (3), (4), (5)식의 常數 $K(A, B, C, D, I)$ 는 (6), (7), (8)식의 常數 $K_i(A_i, B_i, C_i, D_i, I_i)$ 와 다음과 같은 관계를 갖는다.

$$K = \frac{X_1K_1 + X_2K_2}{X_1X_2} \quad (9)$$

混合熱데이터로부터 얻은 (1)식을 利用하여 Van Ness의 方法⁸⁾에 따라 各 溫度에서 組成에 따르는 $\overline{\Delta H}_1^E$ 및 $\overline{\Delta H}_2^E$ (Table 3)를 구하며 (6)식의 係數 A_i, B_i, C_i, D_i 를 얻는다.

한편 係數 I_i 는

$$\begin{aligned} \overline{\Delta G}_i^E/RT = \ln \gamma_i = \ln \frac{Y_i P}{X_i P_1} \\ + \frac{(B_{11} - V_1^L)(P - P_1) + P Y_2^2 \delta_{12}}{RT} \end{aligned} \quad (10)$$

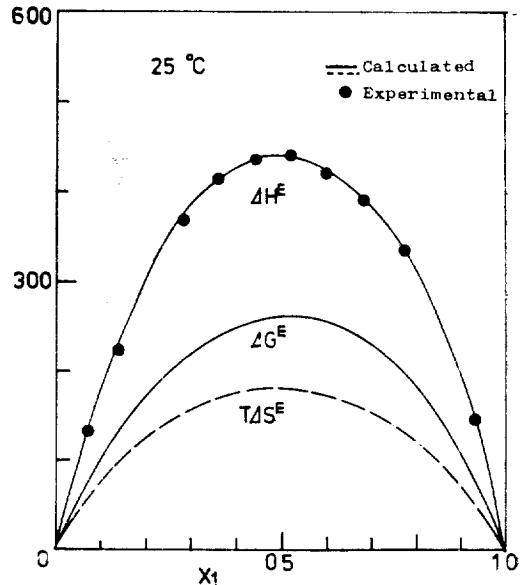
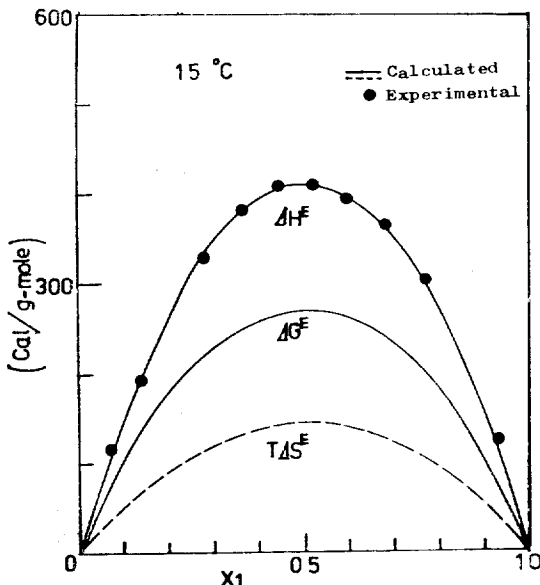


Fig. 2a. Excess Thermodynamic Properties for the 1,2-Dichloroethane(1)-n-Heptan(2) System

Table 3. Partial Excess Heat of Mixing for the 1,2-Dichloroethane(1)-n-Heptane(2) System

	15°C		25°C		35°C		45°C	
X_1	\bar{H}_1^E	\bar{H}_2^E	\bar{H}_1^E	\bar{H}_2^E	\bar{H}_1^E	\bar{H}_2^E	\bar{H}_1^E	\bar{H}_2^E
0.0765	1398.08	6.31	1602.02	11.39	1807.84	20.02	2124.76	28.86
0.1386	1241.95	25.34	1370.41	39.46	1497.85	57.03	1690.71	80.56
0.2795	862.82	126.49	894.01	164.98	966.33	196.29	1006.97	257.96
0.3620	666.10	219.28	675.18	267.94	720.23	312.22	724.50	390.68
0.4408	509.21	324.28	514.14	375.48	534.41	436.33	530.49	519.86
0.5187	384.37	439.17	396.18	483.80	404.13	555.65	411.90	627.96
0.5995	281.75	569.71	305.88	598.01	320.25	661.00	352.01	202.51
0.6819	197.42	719.66	232.15	729.82	267.81	754.17	323.57	753.01
0.7683	122.88	917.46	159.36	924.16	214.46	898.10	279.48	874.52
0.9296	16.86	1551.80	25.92	1751.37	46.81	2012.58	64.85	2332.61

Partial Excess Heat of Mixing for the 1,2-Dichloroethane(1)-n-Butanol(2) System

	15°C		25°C		35°C		45°C	
X_1	\bar{H}_1^E	\bar{H}_2^E	\bar{H}_1^E	\bar{H}_2^E	\bar{H}_1^E	\bar{H}_2^E	\bar{H}_1^E	\bar{H}_2^E
0.1886	620.15	42.68	668.20	62.32	759.61	85.94	900.38	102.50
0.2764	753.35	3.02	856.80	5.78	926.24	36.02	981.25	78.37
0.3492	775.73	-6.30	891.95	-8.36	939.53	31.94	950.03	94.24
0.4219	704.43	39.83	794.69	54.56	817.23	110.61	811.73	182.05
0.5028	568.90	157.38	611.67	213.18	614.74	285.68	617.72	349.80
0.5993	423.06	335.40	427.16	437.49	432.48	505.99	461.93	537.17
0.6998	337.58	491.49	345.59	583.39	377.52	601.19	427.40	595.42
0.7897	277.12	673.23	307.32	699.76	358.31	663.54	405.55	668.22
0.8426	219.19	936.87	254.93	939.02	303.72	914.37	339.76	969.97
0.9197	94.72	1913.68	116.33	2038.51	140.77	2211.67	154.50	2440.31

Partial Excess Heat of Mixing for the n-Heptane(1)-n-Butanol(2) System

	15°C		25°C		35°C		45°C	
X_1	\bar{H}_1^E	\bar{H}_2^E	\bar{H}_1^E	\bar{H}_2^E	\bar{H}_1^E	\bar{H}_2^E	\bar{H}_1^E	\bar{H}_2^E
0.0911	223.82	2.62	294.16	3.99	396.01	6.17	456.69	5.45
0.1837	231.48	1.14	310.45	0.98	384.01	3.13	489.49	-0.30
0.2701	233.38	0.86	316.56	-0.36	391.56	1.49	495.07	-1.12
0.3592	208.73	12.62	280.40	16.93	345.72	23.49	429.78	29.96
0.4520	166.75	41.53	218.17	59.76	267.92	76.90	326.58	100.82
0.5412	130.01	77.64	166.51	110.39	206.17	137.18	247.99	177.57
0.6290	107.01	109.72	139.04	148.37	177.85	176.18	214.17	223.80
0.7214	91.88	141.33	126.08	175.30	168.07	196.51	205.26	242.22
0.8293	64.58	242.10	94.59	273.91	129.94	342.24	160.93	412.87
0.9125	27.94	503.80	42.36	669.31	58.81	854.63	73.26	1045.19

Table 4a. Constants of the Equation(6) (7) (8) for the 1,2-Dichloroethane(1) (1,2-Dichloroethane-n-Heptane System)

X_1	$A_1(-)$	$B_1(^{\circ}\text{K}^{-1})$	$C_1(^{\circ}\text{K}^{-2})$	$D_1(^{\circ}\text{K})$	$I_1(-)$
0.0765	2491.65	-16.65	0.0279	-248635.69	12963.01
0.1386	1493.05	-9.97	-0.3586	-148939.64	7768.90
0.2795	-1687.45	1.13	-5.6716	170582.57	-8797.33
0.3620	-1772.05	11.72	-5.8124	178738.48	-9234.82
0.4408	-906.60	6.01	-1.9059	91312.33	-4722.53
0.5187	88.72	-0.57	4.1529	8999.22	464.50
0.5995	622.24	-4.12	8.5112	-62560.74	3242.39
0.6819	428.77	-2.87	6.0282	-42745.64	2230.09
0.7683	-220.87	1.40	-5.4494	22947.75	-1158.56
0.9296	-345.06	2.26	0.7313	35014.07	-1801.09

Constants of the Equation(6) (7) (8) for the n-Heptane(2) (1,2-Dichloroethane-n-Heptane System)

X_1	$A_2(-)$	$B_2(^{\circ}\text{K}^{-1})$	$C_2(^{\circ}\text{K}^{-2})$	$D_2(^{\circ}\text{K})$	$I_2(-)$
0.0765	-79.71	0.5193	-0.0008	8117.83	-416.49
0.1386	51.65	-0.3586	0.0006	-5010.22	267.00
0.2795	852.34	-5.6717	0.0095	-85447.87	4437.54
0.3620	871.80	-5.8124	0.0097	-87236.03	4537.38
0.4408	279.60	-1.9059	0.0033	-27417.58	1449.75
0.5187	-636.36	4.1529	-0.0067	64889.81	-3323.59
0.5995	-1291.61	8.5112	-0.0140	130656.40	-6735.10
0.6819	-908.11	6.0282	-0.0010	91437.60	-4729.25
0.7683	836.17	-5.4495	0.0089	-84922.66	-4368.96
0.9296	-143.64	0.7313	-0.0007	17441.98	-776.69

Constants of the Equation(2) (3) (4) (5) for the 1,2-Dichloroethane(1)-n-Heptane(2) System

X	$A(-)$	$B(^{\circ}\text{K}^{-1})$	$C(^{\circ}\text{K}^{-2})$	$D(^{\circ}\text{K})$	$I(-)$
0.0765	1656.10	-11.2454	0.0192	-163116.47	8593.58
0.1386	2105.93	-14.1627	0.0240	-209052.99	10945.35
0.2795	707.45	-4.8390	0.0084	-68961.07	3666.68
0.3620	-369.21	2.3121	-0.0035	39170.84	-1940.44
0.4408	-986.96	6.4251	-0.0104	101091.40	-5156.25
0.5187	-1042.50	6.8168	-0.0111	106403.11	-5442.45
0.5995	-600.82	3.9100	-0.0063	61735.68	-3138.66
0.6819	16.17	-0.1823	0.0005	-285.62	75.27
0.7683	1350.81	-1.0343	0.0021	-11492.40	686.25
0.9296	-5056.00	32.9044	-0.0532	516121.90	-26419.21

Table 4b. Constants of the Equation(6)(7)(8) for the 1,2-Dichloroethane(1)
(1,2-Dichloroethane-n-Butanol System)

X_1	$A_1(-)$	$B_1(^{\circ}\text{K}^{-1})$	$C_1(^{\circ}\text{K}^{-2})$	$D_1(^{\circ}\text{K})$	$I_1(-)$
0.1886	76.31	-0.7061	0.0015	-4713.64	369.14
0.2764	517.36	-3.2661	0.0052	-54431.74	2720.87
0.3492	812.26	-5.0774	0.0079	-86159.43	4278.15
0.4217	991.52	-6.2936	0.0100	-103687.68	5207.26
0.5028	946.77	-6.1456	0.0100	-96909.89	4951.34
0.5993	510.76	-3.4320	0.0058	-50464.74	2653.45
0.6998	-167.80	1.0124	-0.0015	18422.85	-888.90
0.7891	-578.14	3.7886	-0.0062	58715.87	-3017.60
0.8426	-594.14	3.9356	-0.0065	59682.67	-3094.73
0.9197	-306.45	2.0499	0.0034	30473.62	-1593.20

Constants of the Equation(6)(7)(8) for the n-Butanol(2) (1,2-Dichloroethane-n-Butanol System)

X_1	$A_2(-)$	$B_2(^{\circ}\text{K}^{-1})$	$C_2(^{\circ}\text{K}^{-2})$	$D_2(^{\circ}\text{K})$	$I_2(-)$
0.1886	-251.39	1.6743	-0.0028	25076.93	-1307.89
0.2764	-384.09	2.4447	-0.0039	40033.62	-2015.43
0.3492	-517.81	3.2679	-0.0051	54390.84	-2721.29
0.4217	-628.00	4.0182	-0.0064	65122.34	-3291.95
0.5028	-582.35	3.8455	-0.0063	58544.45	-3034.26
0.5993	-28.51	0.3893	-0.0009	-309.93	-116.82
0.6998	1243.52	-7.9530	0.0127	-129280.65	6522.06
0.7891	2411.75	-15.8697	0.0260	-243792.87	12580.36
0.8426	2457.71	-16.3561	0.0272	-245569.90	12792.33
0.9197	95.30	-0.8325	0.0018	-6320.51	468.16

Constants of the Equation(2)(3)(4)(5) for the 1,2-Dichloroethane(1)-n-Butanol(2) System

X_1	$A(-)$	$B(^{\circ}\text{K}^{-1})$	$C(^{\circ}\text{K}^{-2})$	$D(^{\circ}\text{K})$	$I(-)$
0.1886	-1238.90	8.0072	-0.0128	127154.31	-6479.81
0.2764	-674.64	4.3309	-0.0068	69615.93	-3531.55
0.3492	-234.76	1.5565	-0.0025	23368.38	-1219.25
0.4219	226.64	-1.3626	0.0021	-25004.50	1204.86
0.5028	745.99	-4.0123	0.0075	-78474.43	3923.71
0.5993	1227.10	-7.9155	0.0128	-126458.69	6427.12
0.6998	1218.01	-7.9924	0.0131	-123370.83	6358.87
0.7897	304.87	-2.0805	0.0037	-29515.31	1581.54
0.8426	-857.89	5.5923	-0.0090	87735.33	-4479.58
0.9197	-3712.72	24.6231	-0.0406	372624.83	-19331.63

Table 4c. Constants of the Equation(6) (7) (8) for the n-Heptane(1) (n-Heptane-n-Butanol System)

X_1	$A_1(-)$	$B_1(^{\circ}\text{K}^{-1})$	$C_1(^{\circ}\text{K}^{-2})$	$D_1(^{\circ}\text{K})$	$I_1(-)$
0.0911	182.94	-1.2258	0.0021	-18409.73	953.83
0.1837	846.24	-5.6258	0.0094	-85049.46	4408.48
0.2701	836.57	-5.5460	0.0092	-84321.08	4360.30
0.3592	573.37	-3.7926	0.0063	-57957.91	2990.13
0.4520	241.58	-1.5957	0.0027	-24511.33	1260.88
0.5412	-32.42	0.2140	-0.0003	3166.37	-167.83
0.6290	-215.20	1.4220	-0.0023	21592.17	-1120.62
0.7214	-291.21	1.9278	-0.0032	29183.27	-1516.30
0.8293	-223.24	1.4822	-0.0024	22288.96	-1161.73
0.9125	-92.63	0.6166	0.0010	9218.46	-481.81

Constants of the Equation(6) (7) (8) for the n-Butanol(2) (n-Heptane-n-Butanol System)

X_1	$A_2(-)$	$B_2(^{\circ}\text{K}^{-1})$	$C_2(^{\circ}\text{K}^{-2})$	$D_2(^{\circ}\text{K})$	$I_2(-)$
0.0911	-83.84	0.5992	-0.0009	8371.06	-436.20
0.1837	-179.99	1.1965	-0.0020	18037.59	-936.99
0.2701	-172.54	1.1425	-0.0019	17360.11	-898.85
0.3592	-49.07	0.3203	-0.0005	4989.14	-256.06
0.4520	178.25	-1.1847	0.0020	-17929.31	928.78
0.5412	447.82	-2.9651	0.0049	-45159.86	2334.43
0.6290	702.97	-4.6515	0.0077	-70878.04	3664.53
0.7214	853.23	-5.6521	0.0094	-85873.39	4446.65
0.8293	583.75	-3.8829	0.0065	-58583.45	304.24
0.9125	-346.61	2.2854	-0.0037	34481.42	-1801.94

Constants of the Equation(2) (3) (4) (5) for the n-Heptane(1)-n-Butanol(2) System

X_1	$A(-)$	$B(^{\circ}\text{K}^{-1})$	$C(^{\circ}\text{K}^{-2})$	$D(^{\circ}\text{K})$	$I(-)$
0.0911	-719.09	4.7895	-0.0079	71633.77	-3738.74
0.1837	56.88	-0.3784	0.0007	-5998.51	299.89
0.2701	507.35	-3.3638	0.0056	-51251.27	2646.00
0.3592	758.15	-5.0269	0.0084	-76556.58	3953.40
0.4520	835.19	-5.5329	0.0092	-84395.32	4355.70
0.5412	756.79	-5.0123	0.0084	-76542.52	3947.63
0.6290	537.55	-3.5623	0.0060	-54483.78	2805.41
0.7214	137.49	-0.9153	0.0016	-14287.44	721.33
0.8293	-603.87	4.0008	-0.0065	59931.84	-3138.42
0.9125	-1438.51	9.5511	-0.0156	143141.69	-7481.14

$$\overline{\Delta G_2^E}/RT = \ln \gamma_2 = \ln \frac{Y_2 P}{X_2 P_2} + \frac{(B_{22} - V_2^L)(P - P_2) + P Y_1^2 \delta_{12}}{RT} \quad (11)$$

의關係式과 함께 35°C의 P - X 데이터⁹⁾를 利用하여 (7)式과의關係에서 各組成에 해당되는 常數 I_i 를 計算할 수 있다.

計算된 常數 A_i , B_i , C_i , D_i , I_i 값과 (9)式과의關係에서 total property에 해당되는 常數 A , B , C , D , I 를 計算 (Table 4)하였다.

(3), (4), (5)式에서 얻은 ΔH^E , ΔS^E , ΔG^E 에 對한 結果는 total pressure⁹⁾法으로 구한 ΔG^E 값과 아울러 plot (Fig. 2, 3, 4)하였다.

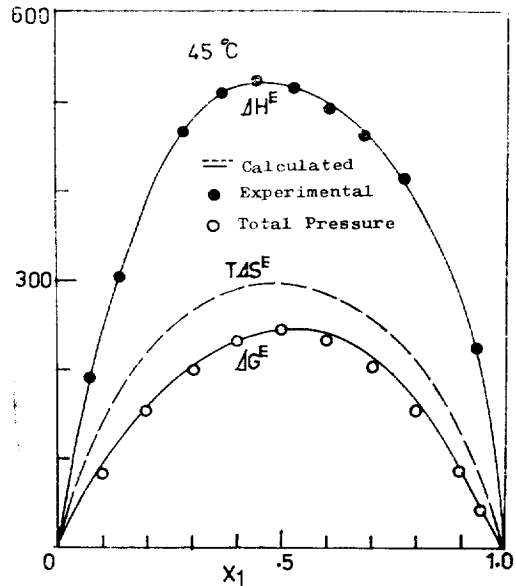
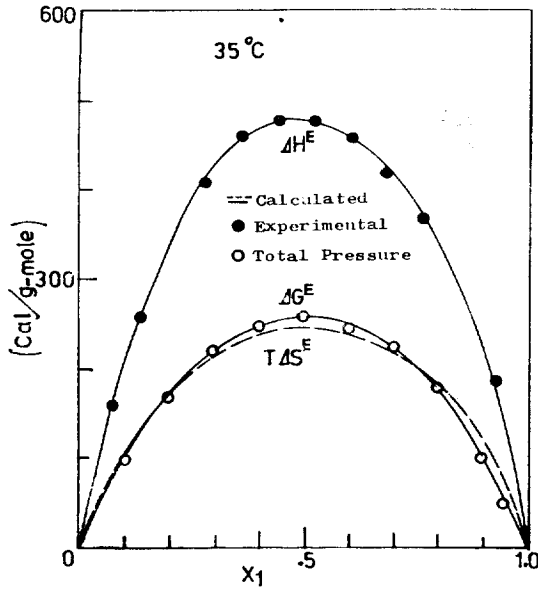


Fig. 2b. Excess Thermodynamic Properties for the 1,2-Dichloroethane(1)-n-Heptane(2) System

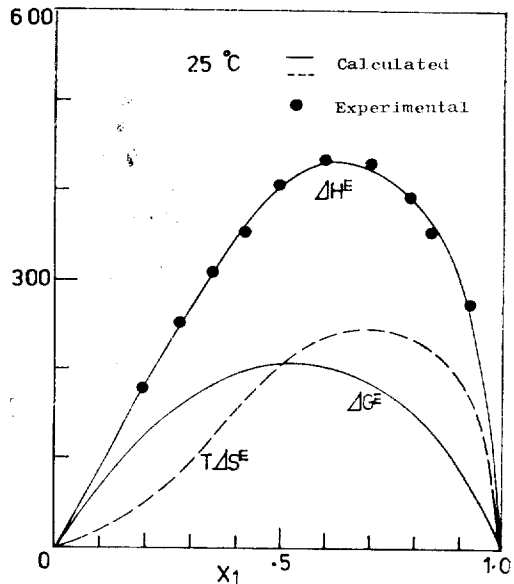
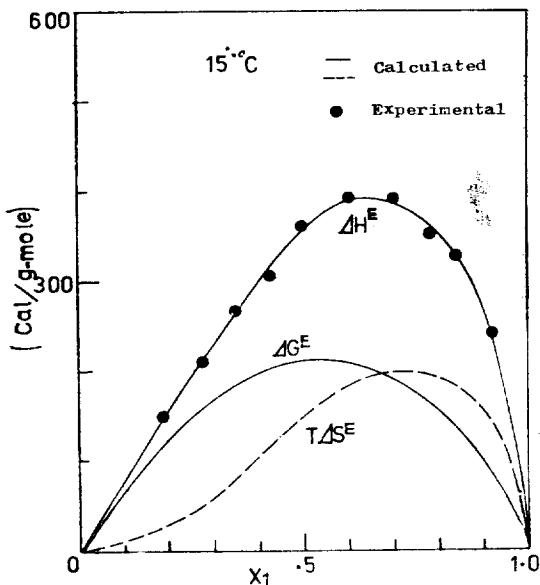


Fig. 3a. Excess Thermodynamic Properties for the 1,2-Dichloroethane(1)-n-Butanol(2) System

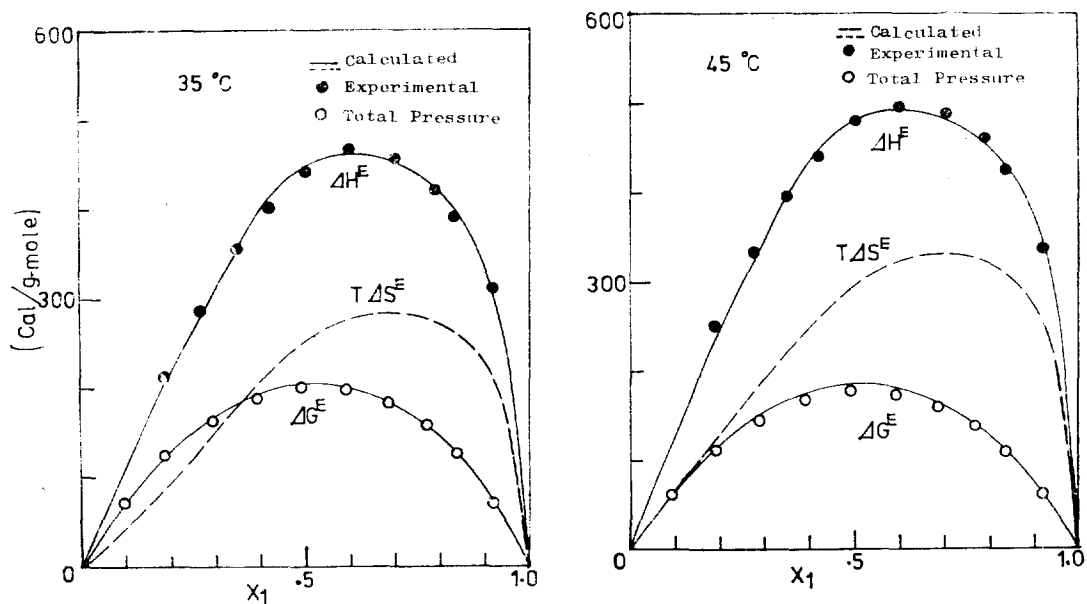


Fig. 3b. Excess Thermodynamic Properties for the 1,2-Dichloroethane(1) n-Butanol(2) System

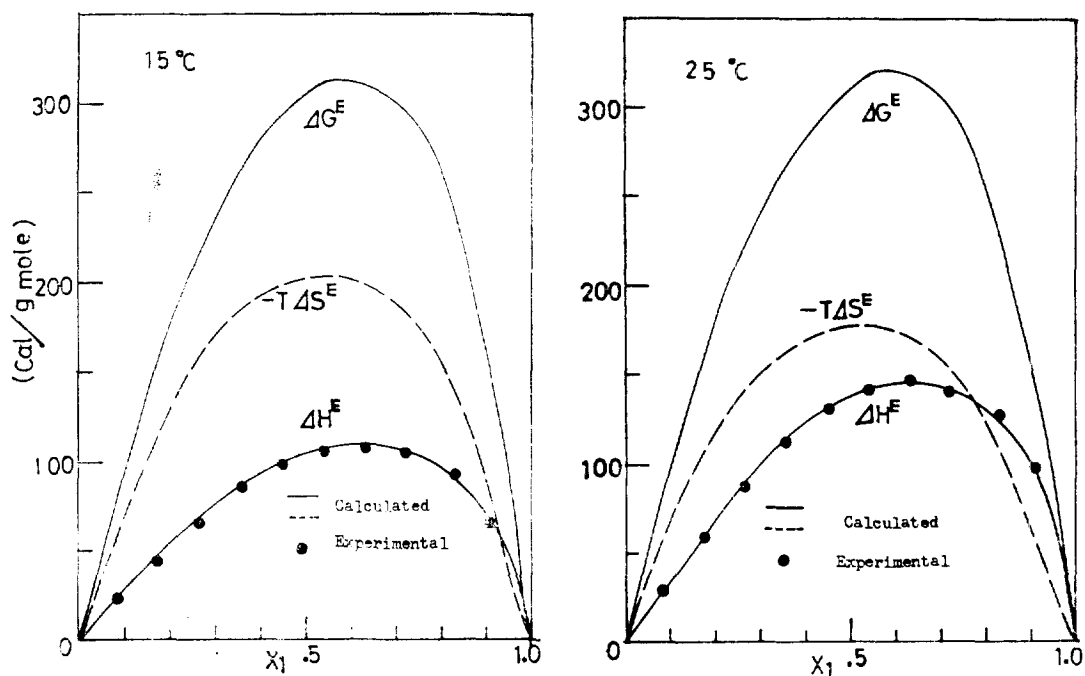


Fig. 4a. Excess Thermodynamic Properties for the n-Heptane(1)-n-Butanol(2) System

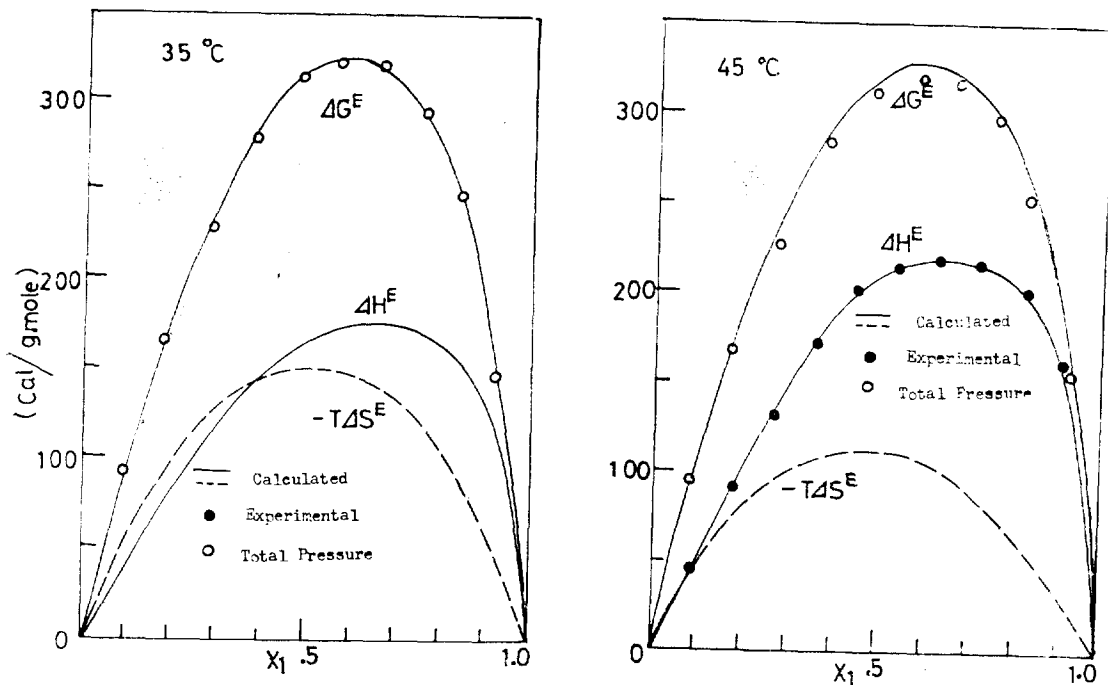


Fig. 4b. Excess Thermodynamic Properties for the n-Heptane(1)-n-Butanol(2) System

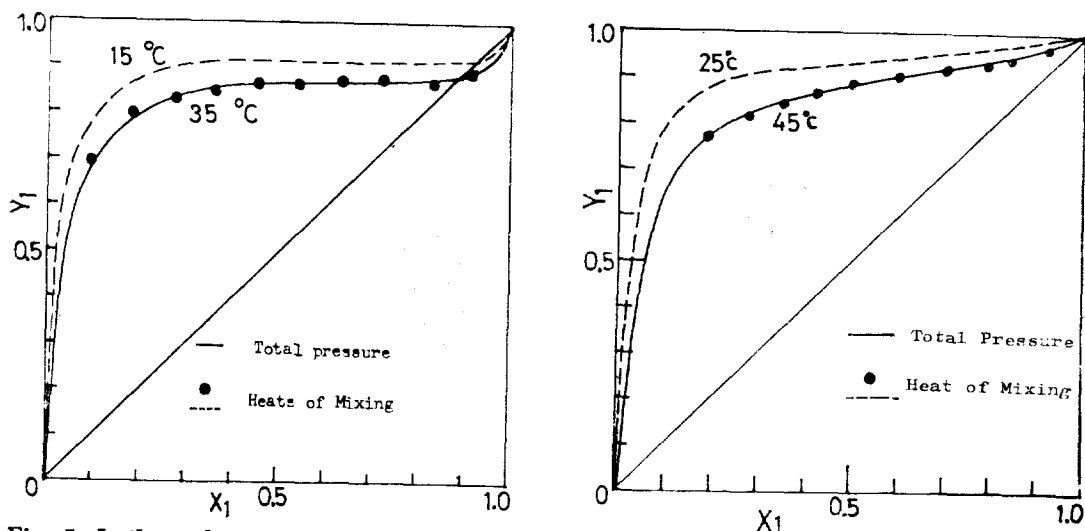


Fig. 5. Isothermal Vapor-Liquid Equilibrium for the 1,2-Dichloroethane(1)-n-Butanol(2) System

3-2 等溫氣液平衡値의 推算

임의의 온도下에서 (10), (11)式을 利用하면 等溫氣液平衡値를 얻을 수 있게 된다. 즉 一定溫度에서 全壓 P 를 變化시켜가면서 $Y_1 + Y_2 = 1$ 을 만족할 때까지 計算을 반복하면 Y 와 P 를 推算

할 수 있다. 이와같이 混合熱로부터 구한 等溫氣液平衡値를 total pressure 法으로 구한 等溫氣液平衡値와 35 °C, 45 °C에서 比較하여 plot 하면 (Fig. 5, 6, 7) 두 결과는 良好한 一致를 나타내고 있다.

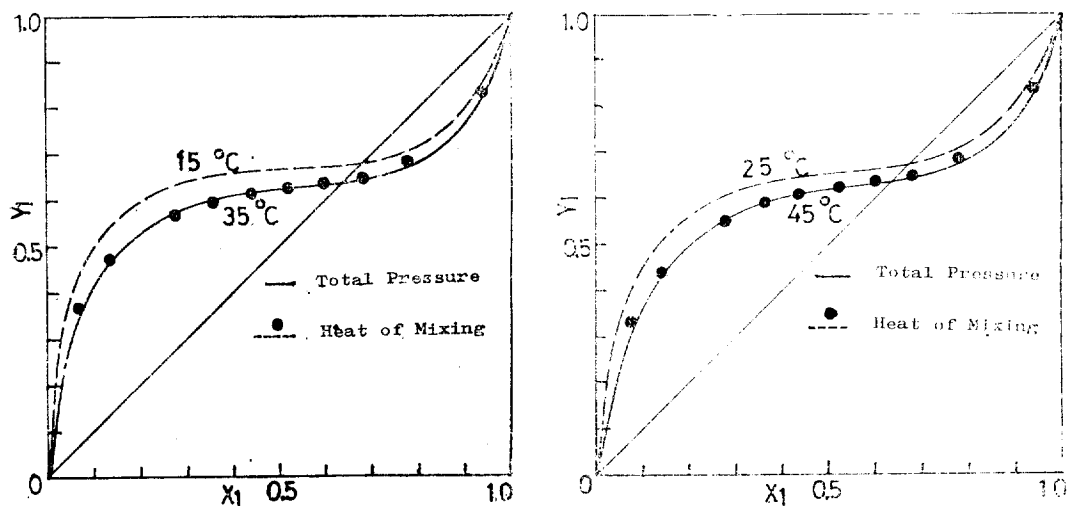


Fig. 6. Isothermal Vapor-Liquid Equilibrium for the 1,2-Dichloroethane(1)-n-Heptane(2) System

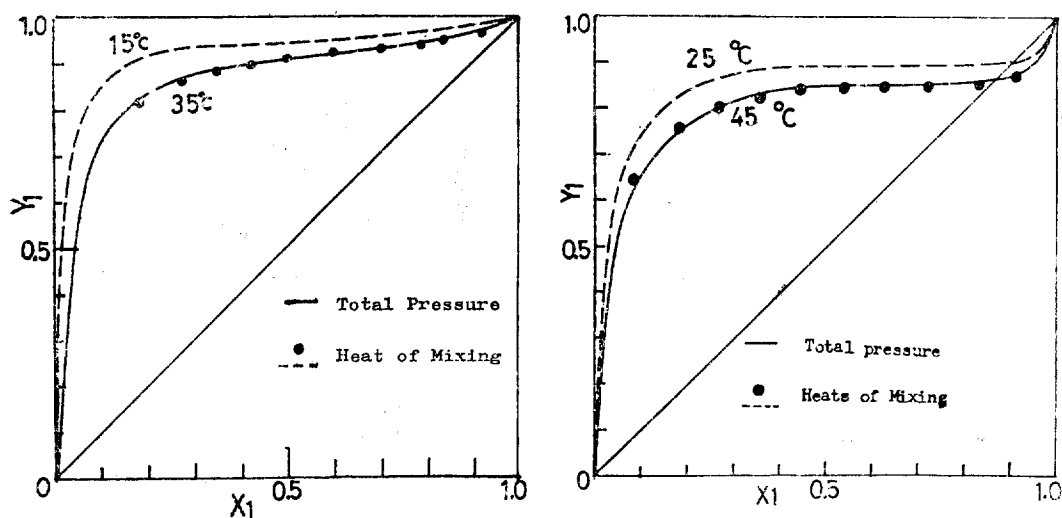


Fig. 7. Isothermal Vapor-Liquid Equilibrium for the n-Heptane(1)-n-Butanol(2) System

3-3 等壓氣液平衡値의 推算

等溫氣液平衡値를 推算하는 方法과 마찬가지로 一定한 P 값을 (10), (11)式에 代入하고 溫度

T 를 變化시켜가면서 $Y_1 + Y_2 = 1$ 을 만족할 때까지 반복計算하여 T 와 Y 를 決定한다. 이때 P 는 150 mmHg와 300 mmHg의 경우를 取하였으며, 그 結果는 Fig. 8과 같다.

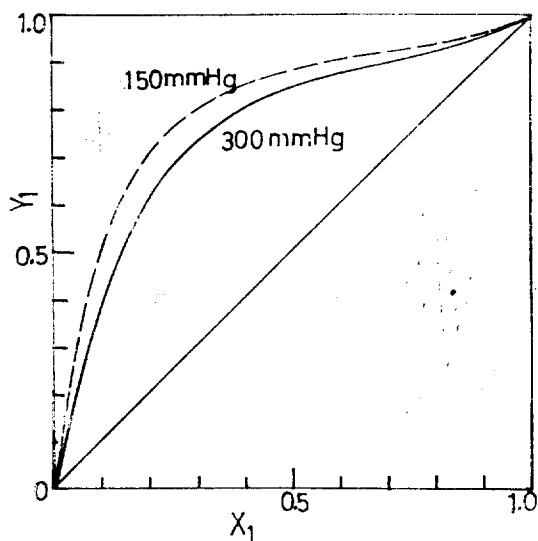


Fig. 8a. Isobaric Vapor-Liquid Equilibrium for the 1,2-Dichloroethane(1)-n-Butanol(2) System

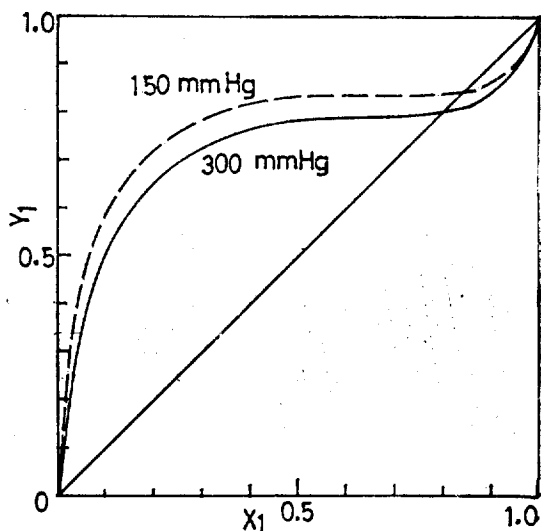


Fig. 8c. Isobaric Vapor-Liquid Equilibrium for the n-Heptane(1)-n-Butanol(2) System.

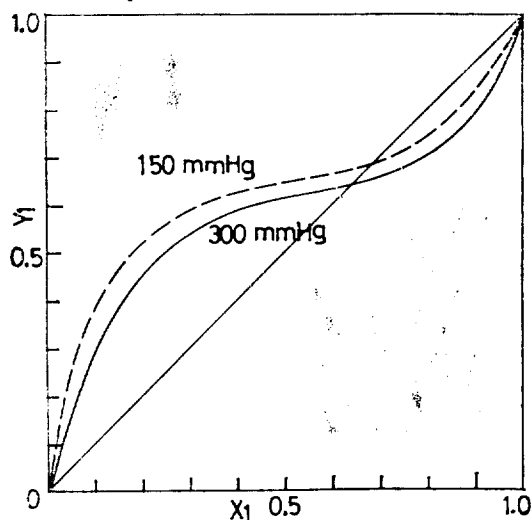


Fig. 8b. Isobaric Vapor-Liquid Equilibrium for the 1,2-Dichloroethane(1)-n-Heptane(2) System

4. 結 論

(1) Fig. 1에서 볼 수 있는 바와 같이 1,2-dichloroethane-n-heptane系 1,2-dichloroethane-n-Butanol系 및 n-heptane-n-butanol系の 혼합熱은 正의 값(吸熱)을 나타내고 溫度가 증가함에 따라 증가하는 경향을 보이고 있다.

(2) partial excess heat of mixing 및 ΔG^E 와 ΔS^E 를 計算하였고, 等溫氣液平衡値를 推算하여 同一한 溫度下에 total pressure法에 依한 等溫氣液平衡値와 比較하여 良好한 一致를 보았다.

(3) 150 mmHg와 300 mmHg에서 等壓氣液平衡値를 推算하였다.

後 記

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使用記號

- a, b, c, d, e Constants of equation(1)
- ΔH^E Heats of mixing(cal./g-mole)
- ΔG^E Excess Gibbs free energy Change of mixing(cal./g-mole)
- ΔC_p Heat Capacity Change of mixing(cal./g-mole $^{\circ}$ K)
- ΔS^E Excess entropy Change of mixing(cal./g-mole $^{\circ}$ K)
- $\overline{\Delta H}_i$ Partial molar heats of mixing(cal./g-mole)

X	Mole fraction of liquid phase
Y	Mole fraction of gas phase
R	Gas constant
T	Temperature($^{\circ}\text{K}$)
A, B, C, D, I	Constant of equation
A_i, B_i, C_i, D_i, I_i	Constants of equation
B_{ii}	Second virial coefficient of the component i ($\text{cm}^3/\text{g-mole}$)
P	Pressure(mmHg)
V_i^L	Molar volume of the liquid phase of the component i ($\text{cm}^3/\text{g-mole}$)
σ_{12}	$2B_{12}-B_{11}-B_{22}$
K	Constant representing A, B, C, D, I
γ_i	Activity coefficient of the component i

참고 문헌

1. J.M. Prausnitz, "Molecular thermodynamics of fluid-phase equilibria" Prentice-Hall, New Jersey, 1969.
2. H.C. Van Ness, C.A. Soczek and N.K. Kochar, *J. of Chem. Eng. Data.*, **12**(1967) 346.
3. R.V. Orye and J.M. Prausnitz, *Ind. Eng. Chem.*, **57**(1965) 18.
4. R.W. Hanks, A.V. Gupta and James Christensen, *Ind. Eng. Chem. Fundam.*, **10**(1971) 540.
5. A.G. Duncan and M.J. Hiza, *Ind. Eng. Chem. Fundam.*, **11**(1972) 38.
6. J.N. Rhim and K.C. Kim, *Hwahak Konghak(Korea)* **15**(1977) 333.
7. J.A. Larkin and M.L. McGlashan, *J. Amer. Chem. Soc.*, **83**(1961) 3425.
8. H.C. Van Ness and R.V. Mrazek, *AIChE J.*, **5**(1959) 209.
9. C. Kwak, *M.S. Thesis* Dep't of Chem. Eng., Graduate School, Han Yang Univ., 1978.

