Table 5 Prediction of Azeotropic Behavior for Toluene (1)-n-Butanol (2) System

Input Data		t_b [°C]	N	S	T	$M^{a)}$			
Toluene (1)		110.625	7.441	+0.02291	-0.00426	92			
<i>n</i> -Butanol (2)		117.73	7.702	-0.6764	-0.1184	74			
x_1	0.55	0.60	0.62	0.64	0.66	0.68	0.70	0.72	
y_{1_0}	0.625	0.645	0.655	0.665	0.675	0.685	0.690	0.700	
t_b	105.75	105.6	105.55	105.5	105.5	105.5	105.5	105.5	
N	7.264	7.259	7.256	7.2555	7.255	7.2545	7.255	7.2555	
S	-0.293	-0.225	-0.218	-0.211	-0.204	-0.197	-0.193	-0.186	
T	-0.0471	-0.0448	-0.0437	-0.426	-0.0414	-0.0403	-0.0397	-0.0386	
x_1	0.74	0.76	0.78	0.80	0.82	0.84	0.86	0.88	
y_{1_0}	0.705	0.715	0.725	0.740	0.755	0.770	0.785	0.800	
t_b	105.55	105.6	105.65	105.75	105.9	106.1	106.35	106.6	
N	7.256	7.259	7.260	7.264	7.269	7.276	7.285	7.294	
S	-0.183	-0.176	-0.169	-0.1585	-0.148	-0.137	-0.127	-0.116	
T	-0.0380	-0.0369	-0.0357	-0.0340	-0.0323	-0.0306	-0.0289	-0.0272	
x_1	0.90	0.92	0.94	0.96	0.98				
y_{1_0}	0.825	0.850	0.880	0.915	0.960				
t_b	106.9	107.3	107.85	108.6	109.55				
N	7.305	7.320	7.340	7.367	7.401				
S	-0.099	-0.082	-0.060	-0.036	-0.004				
T	-0.0243	-0.0215	-0.0180	-0.0141	-0.0089				
Results									
P [mmHg]	1000	600	400	200	100	60	40	20	10
t_b (calc) [°C]	114.6	98.1	86.1	67.5	50.9	39.8	31.4	... ^{b)}	...
w_1 (calc)	0.688	0.744	0.806	0.867	0.884	0.884	0.968	...	...
w_1 (lit)		0.735	0.771	0.832					
a) Molecular weight.		b) Nonazeotrope is predicted.							

- 11) Nakanishi, K., Kurata, M., Tamura, M.: *J. Chem. Eng. Data* 5, 210 (1960)
- 12) Nakanishi, K., Shirai, H.: Abstracts, Nagoya Meeting of the Society of Chemical Engineers. Japan, p. 39, Oct. 1965.
- 13) Othmer, D. F., Huang, H.-N.: *Ind. Eng. Chem.*, 57 [10] 42 (1965)
- 14) Reid, R. C., Sherwood, T. K.: "Properties of Gases and Liquids, Their Estimation and Correlation", 2nd. Ed., Chapter 4, McGraw-Hill, 1966
- 15) Robinson, E., Wright, W. A., Bennett, G. W.: *J. Phys. Chem.* 36, 658 (1932)
- 16) Yamada, I. in "Bussei-Teisu 1965", p. 3, Maruzen. Tokyo, 1965
- 17) Zwolinski, B. J., Wilhoit, R. C.: private communication. Oct. 1967

VAPOR-LIQUID EQUILIBRIA FOR BINARY AND TERNARY SYSTEMS CONTAINING CARBON DIOXIDE*

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Vapor-liquid equilibria containing carbon dioxide: $\text{CO}_2\text{-CO}$, $\text{CO}_2\text{-Ar}$, $\text{CO}_2\text{-CH}_4$ and $\text{CO}_2\text{-H}_2\text{-CO}$ were measured by static method at -50°C to 20°C and up to 200 atm. By using these data and the data available in literature, the extent of usefulness of the Benedict-Webb-Rubin equation (hereafter abbreviated as BWR equation) and the treatment of Leland et al. were studied. The BWR equation correctly predicted the vapor-liquid equilibria of inorganic mixtures except in the critical region, while the treatment of Leland et al. was insufficient.

Introduction

In a previous paper¹²⁾, vapor-liquid equilibria were investigated for the purpose of obtaining fundamental

data that may be useful for the separation of carbon dioxide mixture by liquefaction. As a continuation, the $\text{CO}_2\text{-CO}$, $\text{CO}_2\text{-Ar}$, and $\text{CO}_2\text{-CH}_4$ binary systems were further investigated. To investigate the possibility of

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Fig. 1 Schematic diagram of the experimental apparatus

Table 1 Experimental Results for the CO_2 -CO system

Temp. [°C]	Press. [atm]	x_{CO}	y_{CO}
-50	23.6	—	0.652
	49.1	—	0.777
	94.2	0.223	0.787
-40	119.7	0.323	0.755
	27.5	—	0.606
	53.4	0.101	0.707
	90.7	0.204	0.733
	116.0	0.298	0.705
-20	125.6	0.347	—
	129.1	0.369	0.647
	52.0	0.082	0.501
	80.8	0.155	0.577
	98.5	0.213	0.576
0	116.0	0.288	0.552
	61.2	0.066	0.299
	80.8	0.124	0.371
	98.5	0.191	0.375
10	104.4	0.228	0.356
	61.2	0.043	0.173
	80.8	0.102	0.257
	90.7	0.142	0.265
	94.4	0.165	0.257

using carbon dioxide as a solvent for separating a CO - H_2 mixture, the CO_2 - H_2 - CO ternary system was also studied.

By using these data, the Benedict-Webb-Rubin equation of state and the treatment of Leland et al. were examined to see to what extent they are useful for the prediction of the vapor-liquid equilibria of inorganic mixtures.

1. Experimental Procedure

The equilibrium apparatus used in the present work was described in detail in the previous paper¹²⁾. In brief, this apparatus consists of a methanol bath containing an equilibrium cell and a gas analysis system, as shown in Fig. 1.

Carbon dioxide was first introduced into the cell and then a solute gas up to a given pressure. This mixture was agitated by moving three disk plates magnetically up and down for three to four hours until complete equilibrium was reached.

Vapor and liquid samples were sent individually to the gas analysis system and their compositions were determined by volumetric method. Carbon dioxide of the binary system was absorbed into a KOH solution and carbon monoxide of the ternary system into a cuprammonium solution with sulfuric acid which absorbed the generated ammonium vapor simultaneously. It was experimentally ascertained that the amount of the remaining gas thereby absorbed was within the accuracy of the experiments.

Argon used in this study was furnished by Nippon Sanso Industry Co., Ltd. with purity of 99.99 mole percent. Methane and carbon monoxide were supplied by Takachiho Chemical Industry Co., Ltd. and their purities were more than 99.9 mole percent and 99.8 mole percent, respectively.

2. Results and Discussion

The experimental results are summarized in Tables 1 to 4. Each data point is an average of four to five measurements and the deviation from the average value is within one percent. The same straight line correlations as for liquid-liquid equilibria⁸⁾ are illustrated for the ternary system (Fig. 2) and the binary system (Fig. 3).

In the previous paper¹²⁾, it was shown that the experimental data agreed well with those of other authors for the CO_2 - N_2 and CO_2 - O_2 systems. But slight differences from interpolated data of Donnelly and Katz⁶⁾ are observed for the CO_2 - CH_4 system as shown in Fig. 10.

2-1. Relative volatility of H_2 to CO Though the liquefaction of carbon monoxide is one of the useful method for separating a CO - H_2 mixture, extremely low temperature is needed. Then carbon dioxide may be chosen

Fig. 2 Straight line correlation for the $\text{CO}_2\text{-H}_2\text{-CO}$ system

Fig. 3 Straight line correlation for the $\text{CO}_2\text{-Ar}$ system

Table 2 Experimental Results for the $\text{CO}_2\text{-Ar}$ system

Temp. [°C]	Press. [atm]	x_{Ar}	y_{Ar}
-40	25.4	—	0.552
	43.2	—	0.683
	60.6	0.120	0.734
	97.5	0.216	0.754
-20	130.6	0.350	0.706
	43.2	0.053	0.454
	60.6	0.095	0.548
	97.5	0.205	0.613
0	121.0	0.295	0.582
	128.6	—	0.548
	43.2	—	0.149
	49.0	0.033	0.211
10	60.6	0.061	0.301
	78.2	0.106	0.383
	97.5	0.171	0.411
	107.2	0.214	0.396
	112.7	0.252	0.378
	114.8	0.282	0.352
115.2	0.310	0.324	

as an extractive solvent for the purpose of relieving this severe condition. Fig. 4 shows the possibility of using carbon dioxide as an extractive solvent in the separation of hydrogen from carbon monoxide, though a relatively large amount of carbon dioxide may be required in practice.

2-2. Comparison of predictions by BWR equation with experimental data The BWR equation for a single-

Table 3 Experimental Results for the $\text{CO}_2\text{-CH}_4$ system

Temp. [°C]	Press. [atm]	x_{CH_4}	y_{CH_4}
-40	36.5	—	0.657
	52.0	0.251	0.717
	61.2	0.360	0.727
	67.2	0.450	—
	71.0	0.519	0.703
-20	36.5	—	0.396
	52.0	0.150	0.515
	61.2	0.213	0.556
	71.0	0.294	0.566
	77.0	0.357	0.563
0	80.0	0.400	0.540
	52.0	0.070	0.254
	61.2	—	0.322
	76.0	0.204	0.370
	80.8	0.246	0.367
10	61.2	0.069	0.188
	71.0	0.115	0.240
	80.8	0.177	0.250

Table 4 Experimental Results for the $\text{CO}_2\text{-H}_2\text{-CO}$ system

x_{CO_2}	x_{H_2}	y_{CO_2}	y_{H_2}
-40°C 100atm			
0.841	0.017	0.226	0.219
0.866	0.018	0.217	0.284
0.888	0.021	0.207	0.373
0.907	0.023	0.194	0.468
0.938	0.026	0.179	0.638
0.938	0.027	0.174	0.644
-20°C 100atm			
0.865	0.021	0.368	0.215
0.906	0.028	0.342	0.379
0.916	0.034	0.332	0.461
0.923	0.032	0.333	0.468
0°C 100atm			
0.846	0.015	0.595	0.066
0.854	0.017	0.589	0.084
0.895	0.029	0.560	0.203
0.898	0.030	0.556	0.214
0.938	0.037	0.539	0.358
10°C 100atm			
0.844	0.013	0.726	0.030
0.874	0.023	0.698	0.077
0.904	0.033	0.678	0.157
0.935	0.042	0.658	0.265
-20°C 50atm			
0.944	0.005	0.506	0.123
0.949	0.006	0.509	0.152
0.971	0.011	0.490	0.356
0.975	0.012	0.493	0.399
-20°C 150atm			
0.677	0.042	0.442	0.104
0.753	0.048	0.363	0.213
0.857	0.057	0.292	0.454
0.919	0.057	0.256	0.662
-20°C 200atm			
0.527	0.141	0.517	0.145
0.656	0.101	0.426	0.214
0.746	0.090	0.343	0.336
0.831	0.088	0.284	0.503

component system is commonly written as¹³

$$p = RTd + \left(B_0 RT - A_0 - \frac{C_0}{T^2} \right) d^2 + (bRT - a) d^3 + aad^6 + \frac{cd^3}{T^2} (1 + rd^2) e^{-rd^2} \quad (1)$$

Benedict, Webb and Rubin have shown that Eq.(1) holds also for a mixture by replacing the above constants by²⁾

Fig. 4 Relative volatilities of H₂ to CO in CO₂ solution

Fig. 5 p-x diagram for the CO₂-H₂ system

$$\begin{aligned}
 A_0 &= \left(\sum_i x_i A_{0i}^{1/2} \right)^2 & B_0 &= \sum_i x_i B_{0i} & C_0 &= \left(\sum_i x_i C_{0i}^{1/2} \right)^2 \\
 a &= \left(\sum_i x_i a_i^{1/3} \right)^3 & b &= \left(\sum_i x_i b_i^{1/3} \right)^3 & c &= \left(\sum_i x_i c_i^{1/3} \right)^3 \\
 \gamma &= \left(\sum_i x_i \gamma_i^{1/2} \right)^2 & \alpha &= \left(\sum_i x_i \alpha_i^{1/3} \right)^3
 \end{aligned} \quad (2)$$

where the subscript i refers to the component i , and

Fig. 6 p-x diagram for the CO₂-N₂ system

this combination rule is also used for a vapor mixture. This equation has been extensively and successfully used to predict P - V - T relations and vapor-liquid equilibria^{2,4 7,19}.

The values of the constants for the BWR equation used in the present investigation are listed in **Table 5**. In the binary systems temperature and pressure were fixed to find the compositions of vapor and liquid phase. In the ternary systems temperature, pressure, and liquid phase composition of the lightest component were fixed.

2-2-1. CO₂-H₂, CO₂-N₂, and CO₂-CO systems In **Figs. 5 to 7** the experimental equilibrium points for these systems are compared with the border curves predicted by the BWR equation. Except in the region near the critical point, the experimental and calculated values agree very well.

2-2-2. CO₂-Ar system **Fig. 8** shows the comparison between theoretical and experimental results. Agreement is good in the vapor phase but somewhat poor in the liquid phase. The constants used for argon are determined at its normal boiling point²⁵. It is important to specify the condition under which constants are determined. For instance, the use of constants for argon determined in the superheated region yielded a greater discrepancy, especially in the liquid phase.

Table 5 Constants for BWR equation

	CH ₄ ¹⁾	C ₃ H ₆ ³⁾	C ₃ H ₈ ¹⁾	<i>n</i> -C ₄ H ₁₀ ¹⁾	N ₂ ²¹⁾	CO ¹⁹⁾	H ₂ ¹⁶⁾	Ar ²⁵⁾	CO ₂ ^{5,23)}
A_0	1.85500	6.11220	6.87225	10.0847	1.19250	1.34122	0.15516743	0.823430	2.7342
B_0	0.0426000	0.0850647	0.0973130	0.124361	0.0458000	0.0545425	0.02084769	0.0222837	0.04987
C_0	22570.0	439182.0	508256.0	992830.0	5889.07	8562.09	359.17609	11049.412	138407.1
a	0.0494000	0.774056	0.947700	1.88231	0.0149000	0.03665	0.001632328	0.02883766	0.13655
b	0.00338004	0.0187059	0.0225000	0.0399983	0.00198154	0.00263158	*	0.00215311	0.004119
c	2545.00	102611.0	129000.0	316400.0	548.064	1040.0	7.27202995	798.295	14889.94
α	0.000124359	0.000455696	0.000607175	0.00110132	0.000291545	0.0001350	0.000116579	0.000035594	0.0000845
γ	0.0060000	0.01829	0.0220000	0.0340000	0.00750000	0.006000	0.00350775	0.0023385	0.005387

* 0.00033838 + 0.00326475/RT

Fig. 7 p - x diagram for the CO_2 -CO system

Fig. 8 p - x diagram for the CO_2 -Ar system

Table 6 Critical constants for N_2 , CO , and O_2 ¹³⁾

	T_c [°K]	P_c [atm]	V_c [l/g-mole]
N_2	126.2	33.5	0.0901
CO	133.0	34.5	0.0931
O_2	154.8	50.1	0.0780

2-2-3. CO_2 - O_2 system The constants for oxygen were recently reported²⁰⁾. Although these constants are useful for the prediction of P - V - T relation, they were unable to yield correct values when applied to the prediction of vapor-liquid equilibria, because of the negativity of α . In order to find a consistent set of constants, the following procedure was taken. Eq. (1) can be written in a reduced form as⁹⁾

$$p_r = \frac{T_r}{V_{ri}} + \frac{B_{0r}T_r - A_{0r} - C_{0r}/T_r^2}{V_{ri}^2} + \frac{b_r T_r - a_r}{V_{ri}^3} + \frac{a_r \alpha_r}{V_{ri}^6} + \frac{c_r}{V_{ri}^3 T_r^2} \left(1 + \frac{\gamma_r}{V_{ri}^2} \right) e^{-\gamma_r/V_{ri}^3} \quad (3)$$

where

$$\begin{aligned} A_{0r} &= \frac{p_c}{R^2 T_c^2} A_0 & B_{0r} &= \frac{p_c}{R T_c} B_0 & C_{0r} &= \frac{p_c}{R^2 T_c^4} C_0 \\ a_r &= \frac{p_c^2}{R^3 T_c^3} a & b_r &= \frac{p_c^2}{R^2 T_c^2} b & c_r &= \frac{p_c^2}{R^3 T_c^3} c \\ \gamma_r &= \frac{p_c^3}{R^2 T_c^2} \gamma & \alpha_r &= \frac{p_c^3}{R^3 T_c^3} \alpha \end{aligned} \quad (4)$$

and the subscript c stands for "critical".

The left hand sides of Eq. (4) were first evaluated for nitrogen by using the constants listed in Table 5 and the criticals¹³⁾. The constants for oxygen were then calculated from these results and related criticals. For comparison, similar treatment was applied to carbon monoxide. The results based on these sets of constants are shown in Fig. 7 and Fig. 9. Agreement with the data is good for the CO_2 -CO system but not in the liquid

Fig. 9 p - x diagram for the CO_2 - O_2 system

phase of the CO_2 - O_2 system. Table 6 suggests that the critical constants of a concerned substance must be close to those of a reference in order for this procedure to be successful.

2-2-4. CO_2 - CH_4 system A large discrepancy between calculated and experimental results has been observed in this system, as shown in Fig. 10. Joffe and Zudkevitch¹⁰⁾ have pointed out that the combination rule similar to Eq. (2) for the constants in the Redlich-Kwong equation cannot yield satisfactory results for carbon dioxide-light hydrocarbon mixtures because of the existence of interaction effects.

Stotler and Benedict²¹⁾ have proposed a modified com-

Fig. 10 p - x diagram for the CO_2 - CH_4 system

Fig. 11 Density of the CO_2 - CH_4 system

bination rule for A_0 as follows

$$A_0 = x_1^2 A_{01} + 2x_1 x_2 m \sqrt{A_{01} A_{02}} + x_2^2 A_{02} \quad (5)$$

The coefficient m for the CO_2 - CH_4 system is given in Table 7 together with those for other systems. The factor m is almost independent of temperature, pressure, and the kind of hydrocarbon, the overall arithmetical mean being 0.88. Fig. 10 shows that present modification improves the degree of agreement except in the critical region. On the other hand, the correct P - V - T relation could not be successfully predicted by introducing m as shown in Fig. 11.

2-2-5. CO_2 - H_2 - CO system The calculated border curve and tie line are shown by full lines in Fig. 12. Agreement with the data is satisfactory except for the tie line.

2-2-6. n - C_4H_{10} - CH_4 - CO_2 system Fig. 13 shows for the data by Wang and Mcketta²². The original com-

Fig. 12 Vapor-liquid equilibria for the CO_2 - H_2 - CO system

Fig. 13 Vapor-liquid equilibria for the n - $\text{C}_4\text{H}_{10}(1)$ - $\text{CH}_4(2)$ - $\text{CO}_2(3)$ system

Table 7 Correction factor, m , for carbon dioxide-hydrocarbon systems

Systems	Temp. [°C]	Press. [atm]	m [—]
CO_2 - CH_4	10.0	71.0	0.920
		80.8	0.850
	-40.0	36.5 61.2	0.893 0.908
CO_2 - C_3H_8 ¹⁸⁾	37.8	34.0 54.4	0.840 0.870
CO_2 - C_3H_6 ²³⁾	0.0	19.6	0.883 ²³⁾
CO_2 - n - C_4H_{10} ¹⁷⁾	104.4	34.0	0.850
		68.0	0.880

bination rule cannot be applied successfully to the ternary systems of carbon dioxide and hydrocarbons. This failure is to be expected from the previous cases of the binary systems.

When the modifier m is known for each of the binary systems, A_0 for a ternary system may be corrected for the following equation²⁴⁾

$$A_0 = x_1^2 A_{01} + x_2^2 A_{02} + x_3^2 A_{03} + 2(x_1 x_2 m_{12} \sqrt{A_{01} A_{02}} + x_1 x_3 m_{13} \sqrt{A_{01} A_{03}} + x_2 x_3 m_{23} \sqrt{A_{02} A_{03}})$$

$$+ x_2 x_3 m_{23} \sqrt{A_{02} A_{03}} \quad (6)$$

The results based on Eq. (6) are shown by chain lines in Fig. 13. Most of the discrepancy has been removed but some still remains in the tie line. The remaining discrepancy can also be removed by introducing m_{123} into the b in Eq. (2) in the form

$$6 x_1 x_2 x_3 m_{123} (b_1 b_2 b_3)^{1/3} \quad (7)$$

where m_{123} was taken as 1.30 for the present system at $x_{CH_4}=0.0665$. The full line shows how closely this correction brings the calculation to the experimental tie line. It should be noted that the factor m_{123} depends on temperature and pressure, and therefore must be experimentally determined for each condition of interest.

2-3. Comparison of experimental data with prediction by the method of Leland et al.

Leland et al.^{14,15} have derived pseudocriticals for both gas and liquid mixtures in the form

$$T_c' = \left[\frac{\sum_i \sum_j x_i x_j a_i a_j}{\sum_i \sum_j x_i x_j (b_i + b_j)^3} \right]^{1/\alpha}$$

$$p_c' = \frac{T_c' \sum_i x_i z_{ci}}{\sum_i \sum_j x_i x_j (b_i + b_j)^3} \quad (8)$$

where

$$a_i = (z_c T_c'^{\alpha+1} / p_c')_i^{1/2}$$

$$b_i = \frac{1}{2} (z_c T_c' / p_c')_i^{1/3}$$

$$\alpha = 1 + \exp[-10 \{ p / \sum_i x_i p_{ci} - 1 \}^2] \quad (9)$$

They have expressed K -value in term of these criticals by applying the principle of corresponding states to the fugacity coefficient of concerned components¹⁴.

This method has the inherent difficulty that in actually using these pseudocriticals one has first to find an extant substance the criticals of which are the same as the pseudocriticals and then to find the associated equation of state. Neither the existence of such a substance is guaranteed nor the equation of state is necessarily known. The reference chosen in the present analysis is carbon dioxide (carbon monoxide yielded poorer results). Fig. 14 shows comparison of the prediction by this method with the data. Similar results were obtained for the other binary systems except for CO_2-H_2 which did not lend itself to computer analysis. Agreement with the data is better at low temperatures than at high temperatures with the exception of the $CO_2-C_3H_8$ system²³.

The reference to be chosen is usually the one which has the z_c -value closest to the z_c 's of a mixture. This selection rule fails in the case of the $CO_2-C_3H_8$ system²³. According to the present analysis on several systems, the choice of the heaviest component for a reference seems more favorable. At any rate, this method will break down as temperature exceeds any one of the critical temperatures of the components.

Conclusions

1. The vapor-liquid equilibria of the CO_2-CO , CO_2-Ar , CO_2-CH_4 , and the CO_2-H_2-CO systems have been investigated at various temperatures and pressures.

2. The BWR equation correctly predicts the vapor-liquid equilibria of inorganic mixtures except in the cri-

Fig. 14 p - x diagram for the CO_2-CO system

tical region.

3. The treatment by Leland et al. is useful only at low temperatures. The likely causes for this failure are (1) the inadequacy of the use of the radial distribution function of molecules, and (2) the inapplicability of the principle of corresponding states to liquids, both assumed in the derivation of pseudocriticals, or (3) the inapplicability of the expression for α to inorganic mixtures.

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Nomenclature

$A_0, B_0, C_0, a, b, c, \alpha, \gamma$	= constants of the BWR equation	
d	= molar density	[g-mol/l]
m	= correction factor	[—]
p	= pressure	[atm]
R	= gas constant, 0.08207	[l·atm/g-mol·°K]
T	= temperature	[°K]
V	= molar volume	[l/g-mol]
x	= mole fraction of liquid	[—]
y	= mole fraction of vapor	[—]
z	= compressibility factor	[—]
α	= empirical constant in pseudocritical expression	[—]

Subscripts and Superscripts

c	= critical property
i, j	= component i and j
i	= ideal state
$'$	= pseudocritical property
r	= reduced property

Literature cited

- 1) Benedict, M., G.B. Webb & L.C. Rubin: *J. Chem. Phys.*, **8**, 334 (1940)
- 2) Benedict, M., G.B. Webb & L.C. Rubin: *ibid.*, **10**, 747

- (1942)
- 3) Benedict, M., G.B. Webb & L.C. Rubin: *Chem. Eng. Progr.*, **47**, 419 (1951)
 - 4) Benedict, M., G.B. Webb & L.C. Rubin: *ibid.*, **47**, 449 (1951)
 - 5) Cullen, E.J. & K.A. Kobe: *A. I. Ch. E. Journal*, **1**, 452 (1955)
 - 6) Donnelly, H.G. & D.L. Katz: *Ind. Eng. Chem.*, **46**, 511 (1954)
 - 7) Hirata, M. & T. Nakahara: *J. Japan Petrol. Inst.*, **9**, 879 (1966)
 - 8) Ishida, K.: *Bull. Chem. Soc. Japan*, **33**, 693 (1960)
 - 9) Joffe, J.: *Chem. Eng. Progr.*, **45**, 160 (1949)
 - 10) Joffe, J. & D. Zudkevitch: *Ind. Eng. Chem. Fundamentals*, **5**, 455 (1966)
 - 11) Kaminishi, G.: Unpublished data
 - 12) Kaminishi, G. & T. Toriumi: *J. Chem. Soc. Japan, Ind. Chem. Sec. (Kogyo Kagaku Zasshi)*, **69**, 175 (1966)
 - 13) Kobe, K.A. & R.E. Jr. Lynn: *Chem. Revs.*, **52**, 117 (1953)
 - 14) Leland, T.W. Jr., P.S. Chappelaar & B.W. Gamson: *A. I. Ch. E. Journal*, **8**, 482 (1962)
 - 15) Leland, T.W. Jr. & W.H. Mueller: *Ind. Eng. Chem.*, **51**, 597 (1959)
 - 16) Motard, R.L. & E.I. Organick: *A. I. Ch. E. Journal*, **6**, 39 (1960)
 - 17) Olds, R.H., H.H. Reamer, B.H. Sage & W.N. Lacey: *Ind. Eng. Chem.*, **41**, 475 (1949)
 - 18) Reamer, R.H., B.H. Sage & W.N. Lacey: *ibid.*, **43**, 2515 (1951)
 - 19) Schiller, F.C. & L.N. Canjar: *Chem. Eng. Progr. Symp. Ser.*, **49**, No. 7, 67 (1953)
 - 20) Seshadri, D.N., D.S. Viswanath & N.R. Kuloor: *J. Chem. Eng. Data*, **12**, 70 (1967)
 - 21) Stotler, H.H. & M. Benedict: *Chem. Eng. Progr. Symp. Ser.*, **49**, No. 6, 25 (1953)
 - 22) Wang, R.H. & J.J. Mcketta: *J. Chem. Eng. Data*, **9**, 30 (1964)
 - 23) Yorizane, M., S. Yoshimura & H. Masuoka: *Kagaku Kōgaku (Chem. Eng., Japan)*, **30**, 1093 (1966)
 - 24) Yorizane, M., S. Yoshimura, H. Masuoka & N. Shiki: Preprint of local meeting of Soc. Chem. Engrs. Japan (Okayama) Oct. (1965) p.5
 - 25) Zudkevitch, D. & T.G. Kaufmann: *A. I. Ch. E. Journal*, **12**, 577 (1966)

SALT EFFECT OF CALCIUM CHLORIDE IN VAPOR-LIQUID EQUILIBRIUM OF THE ALCOHOL-ACETIC ESTER SYSTEMS*

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Vapor-liquid equilibrium data have been obtained for systems methanol-methyl acetate, ethanol-ethyl acetate and *n*-butanol-*n*-butyl acetate with calcium chloride at atmospheric pressure. Calcium chloride was added up to the saturated concentration. By adding salt, the increase of relative volatility of acetic ester was observed and the azeotropic composition shifted to the higher acetic ester composition in all systems. The solubilities of calcium chloride in these boiling alcohol-acetic ester solutions were shown in figures. It is suggested that the salt effect of calcium chloride may be utilized effectively for the separation of these alcohol-acetic ester mixtures.

The problem of salt effect in vapor-liquid equilibrium has been reported by many investigators. These data were collected and published by Ciparis²². However, most of these data were concerned with the salt effect in the binary systems containing water as a component, and there were few data for organic binary systems.

For the study of salt effect on organic compounds, in the present work the following alcohol-acetic ester systems were chosen as organic systems, i.e., methanol-methyl acetate, ethanol-ethyl acetate and *n*-butanol-*n*-butyl acetate systems. Calcium chloride was used as the additional salt, because calcium chloride is soluble in these alcohols.

Data of vapor-liquid equilibrium at atmospheric pressure were obtained for these alcohol-acetic ester systems with calcium chloride. Concentrations of calcium chloride were saturation and below saturation.

Experimental

The apparatus employed was Smith-Bonner type⁶³ still

* Received on December 4, 1967

which was heated by Nichrome wire wound around. The still volume was about 1 l. The consistency test of this apparatus was made for binary systems water-acetic acid and *n*-propanol-water and these data consisted with the data in literatures^{4,53}. The liquid phase was stirred by magnetic stirrer. The temperature of the boiling liquid in the still was read with a mercury thermometer inserted in a thermometer well. The thermometer was checked by the triple point of benzoic acid and a standard thermometer. All chemicals used in this work were analytical reagent grade.

Acetic ester was introduced into the still and the solubility of calcium chloride in boiling acetic ester was measured. After these procedures alcohol and calcium chloride were added. Thus the concentration of alcohol in the still was increased gradually. In the case of saturation, there were small excess solid calcium chloride in the still. In the case of below saturation, alcohol-acetic ester mixture of high acetic ester composition was introduced into the still and the necessary amount of calcium chloride was added. After vapor and liquid samples were taken, the calcium chloride alcohol solution of a