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Relative volatility of esters in ethyl alcohol-water-ester system.

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UNIVERSITY OF LOUISVILLE

RELATIVE VOLATILITY OF ESTERS
//
IN ETHYL ALCOHOL-WATER-ESTER SYSTEM

A Thesis

Submitted to the Faculty
of the Graduate School
of the University of Louisville
in Partial Fulfillment
of the Requirements
for the Degree of

MASTER OF CHEMICAL ENGINEERING

Department of Chemical Engineering

Yi-Chung Chang
//

June 1949

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RELATIVE VOLATILITY OF ESTERS
IN ETHYL ALCOHOL-WATER-ESTER SYSTEM

Yi-Chung Chang

Approved by the Examining Committee

Director G. C. Williams

W. R. Barnes

R. C. Ernst

June 1949

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ABSTRACT

The relative volatilities of five branch-chained esters with respect to ethyl alcohol in mixtures of ethyl alcohol and water containing small amounts of esters were determined experimentally. The results could be used in the design of distillation columns for ethyl alcohol purification.

For alcohol concentrations of more than 50 mol per cent, the increase of relative volatility of the esters was inversely proportional to the alcohol concentration. For dilute concentrations of less than 30 mol per cent the increase in volatility was very rapid, and the rates of increase were different for different esters. No simple quantitative correlation was established between the changes of relative volatility of ester and the concentration of ethyl alcohol.

INTRODUCTION

In the distillation and purification of ethyl alcohol made from fermented mash, one of the major problems is the removal of volatile impurities which, though present in relatively small amount, greatly influence the quality of the product. Included under this general heading among other volatile compounds, are a large number of esters formed either in the course of fermentation of the mash or during the distillation of the alcohol. The volatility of these esters has been found to be quite abnormal and the present system of purification, which briefly stated, is to remove the high boiling tails by fractionating at high proof and the low boiling heads at low proof was ineffective for their removal. The improvement of the design and operation of the process has long been desired, but as in the case of many other distillation problems, the lack of relative volatility data prevented a rational approach to its solution. To meet this end, this research was undertaken to obtain relative volatility data of different esters under the conditions encountered in alcohol distillation.

Owing to the great difficulties of their isolation and identification, the exact nature of the esters involved in ethyl alcohol distillation have not been exactly established. Literature (1) (2) (3) (4) shows that the kinds of esters were numerous. Structurally both straight chained and branch chained esters were present, derived from alcohol radicals ranging from ethyl to amyl and acid radicals ranging from formic to valeric and covering a boiling point range of from 60°

to 150°C. In order to obtain a general picture, a large number of esters should be selected for this investigation. Since the data for some straight chained esters were obtained by the author in an earlier investigation (5) only the branch chained group was investigated in this work.

HISTORICAL

A thorough search of recent literature failed to reveal material concerning the relative volatility of esters in a ternary system of ethyl alcohol, water, and ester. However, in Young's book entitled "Distillation Principles and Processes" (3) the early work of this problem done by Barbet was reported. According to this source, Barbet made some distillation of mixtures of ethyl alcohol, esters, and water over a wide range of concentrations. Among the esters Barbet used were ethyl formate, methyl acetate, ethyl acetate, ethyl iso-butyrate, ethyl iso-valerate, iso-amyl acetate, and iso-amyl iso-valerate.

Barbet used a value K' , called coefficient of purification to express his results. This coefficient was defined by him as a ratio of k' to K or

$$K' = k'/K$$

where $k' = \frac{\text{percentage by wt. of esters in vapor}}{\text{percentage by wt. of esters in liquid}}$

$K = \frac{\text{percentage by wt. of alcohol in vapor}}{\text{percentage by wt. of alcohol in liquid}}$

His plotted results of K' versus alcohol concentration by volume quoted in Young's book was reproduced in Figure 1. The original book of Barbet was written in French entitled "La Rectification et les colonnes Rectificatrices" published in 1895. Since this book was not available to the author at the time of writing this report, the apparatus and the technique used by Barbet in his work were not known; therefore the comparison of them with the modern apparatus and technique for vapor-liquid equilibrium work was not possible. Moreover, while in modern

distillation calculation mol basis is generally used, Barbet's results were in weight and volume basis. This fact made the direct use and comparison of the results rather difficult.

FIG. 1 PURIFICATION COEFFICIENT CURVE OF BARBET

THEORETICAL

According to Walker, et al (6) "Volatility" of any substance is defined as its partial pressure in the vapor phase which is in equilibrium with the liquid phase, divided by its mol fraction in the liquid phase. This definition can be expressed more compactly by the following equation:

$$v = p/x \dots\dots\dots I$$

where v = Volatility of any substance

p = Partial pressure of that substance in
vapor phase

x = Mol fraction of that substance in
liquid phase

Relative volatility between two substances is defined (6) as the ratio of the volatility of one substance to that of the other. For any two substances in a multi-components system, this relationship can be expressed as:

$$\alpha_{AB} = v_A/v_B \dots\dots\dots II$$

where α_{AB} = Relative volatility of substance A with
respect to substance B

v_A = Volatility of substance A

v_B = Volatility of substance B

Combining equations I and II the following equation for relative volatility is obtained:

$$\alpha_{AB} = v_A/v_B = (p_A/x_A)(x_B/p_B) \dots\dots\dots III$$

By means of equation III, the relative volatility can be calculated if partial pressures and mol fractions are known.

Under ordinary conditions the direct measurement of the

partial pressure of one substance in a vapor mixture is very difficult. However its concentration usually can be determined when the vapors are condensed. Under atmospheric pressure and the boiling temperature of liquid mixtures of this work, the deviation of vapors from ideal gas would not be much and Dalton's law of partial pressure could be assumed to hold true. Then the partial pressure of one substance can be calculated from the known values of total pressure and its mol fraction in the vapor condensate by means of the Dalton's law.

$$P_A = P_T y_A \dots\dots\dots \text{IV}$$

where y_A = Mol fraction of substance A in vapor phase

P_T = Total pressure

Substituting the relationship of equation IV for both substances, the relative volatility can be expressed by the mol fractions in both phases.

$$\begin{aligned} \alpha_{AB} &= (p_A/x_A)(x_B/p_B) \\ &= (P_T y_A/x_A)(x_B/P_T y_B^*) \\ &= (y_A^*/x_A)(x_B/y_B^*) \dots\dots\dots \text{V} \end{aligned}$$

where y^* = Mol fraction in vapor which is in equilibrium with liquid

Equation V was the working equation for this investigation.

In general, the four mol fractions of equation V must be determined for each sample of different composition. For the present case, the quantity of esters present in the mixtures was extremely small, not exceeding one per cent. No practical procedure was found for the determination of the amount of

ethyl alcohol in the mixture. However, simplification was possible by making two assumptions which the conditions justified. First, since the quantity of esters was extremely small, its effect on the volatility of ethyl alcohol should be also very small. With no appreciable error introduced, the ratio x_B/y_B^* for alcohol in equation V could be replaced by the corresponding value obtained from an alcohol water mixture of same concentration without any ester added. This equilibrium data appeared in the literatures (7) (8) and could be used to calculate the x_B/y_B^* . Second, in order to save the labor of running too many determinations it was thought that Henry's law should hold for this small concentration of ester in the mixtures for this work. The law says that the partial pressure over the mixture of a volatile solute dissolved in a solvent is proportional to the concentration of the solute in the mixture or

$$p = K''x$$

where p = Partial pressure of the dissolved substance

x = Mol fraction of the dissolved substance in the mixture

K'' = Constant

If this assumption were true, determinations at one ester concentration only would be enough for the whole range and a large amount of work would be saved. For the purpose of substitution to equation V Henry's law can be combined with Dalton's law as follows:

$$P_T y^* = K'' x$$

$$y^*/x = K''/P_T = K^*$$

This K^* is the equilibrium constant, generally used for vapor-liquid work.

For the purpose of comparing the abnormality of the system and a qualitative test of the consistency of the data, the correction factor for Raoult's law defined by the following equation (9) was calculated:

$$y^*/x = \gamma P_0/P_T$$

where P_0 = Vapor pressure of ester in pure state at boiling temperature of mixture

P_T = Total pressure

γ = Correction factor

For an ideal system, the partial pressure of one substance is equal to the product of its mol fraction in the liquid phase and its vapor pressure in the pure state, the correction factor equals to unity. For real system, the correction factor has values other than unity. The deviation from unity is a measure of the abnormality of the system. For consistent data a plot of γ versus alcohol concentration should be an orderly smooth curve.

EXPERIMENTAL

APPARATUS

The special apparatus used in this research was an equilibrium still, diagrammatically shown in Figure 2. This still was a slight modification of the standard Othmer still (10) (11) (12) which is a one piece, all glass joint recycling apparatus consisting mainly of a still and a condenser so arranged that the vapor can condense and over flow from a small pool back to the still. Vaporization and condensation repeat themselves constantly during the refluxing to insure the equilibrium of the liquid and vapor. The body of the still was made from a 600 ml. Kjeldahl flask which held the liquid sample during distillation. Inside the neck and concentric with it, there was a small glass vapor tube of one half inch diameter, leading from about one inch above the liquid surface in the body to the goose neck of the still. During operation, this vapor tube was jacketed by the hot vapors at the boiling point, and any partial condensation or superheating of the vapors inside this small tube was avoided. Connected to the goose neck of the still was a short ball condenser of about 1½ inch diameter which condensed all the vapors from the still. At the lower end of the condenser was a U-shaped condensate chamber of 20 ml. capacity, receiving all the condensates from the condenser. When the chamber was full with liquid, the condensate would over flow through the connecting tube back to the still, thus completing the cycle. The top of the neck of the still was

FIG. 2.- MODIFIED OTHMER EQUILIBRIUM STILL

open and of standard taper so that it could be stoppered with a ground-to-fit glass stopper. Samples were introduced from here. A tapered glass-mercury thermometer was inserted in the stopper when the stopper was in its place. The bulb of the thermometer was just at the outlet of the vapor. Sampling cocks were provided at the bottoms of the still and the condensate chamber, whereby samples could be conveniently withdrawn at the end of the refluxing. Two vents were provided at places as shown in the diagram whereby constant pressure devices could be connected to the system. The heating of the liquid was effected by means of an internal electrical heater made of nichrome wire. The heater was arranged inside and at the bottom of the still body. Platinum lead wires, sealed in the glass provided connections with outside. Around the upper portion of the pear-shaped body and the neck of the still, an external electrical heater was arranged to keep the system in a thermal equilibrium and the whole flask was insulated with glass wool against heat loss. The heating was controlled by means of two Variac transformers.

PROCEDURES

The general procedure for this work consisted of the distillation of the sample to obtain equilibrium liquids and vapors and the subsequent determination of their compositions. Detailed steps were as follows:

1. Preparation of stock solutions and distillation sample:

In order to obtain uniform concentrations of ethyl alcohol in the equilibrium vapors and residual liquids the volume and initial alcohol concentration of the charge to the still were kept constant. Stock solutions of five different alcohol water ratios were prepared by mixing pure ethyl alcohol containing 92.92 % by weight alcohol of Seagram Super-Rectified grade and distilled water. The following is a list of the dilutions:

Dilution No.	Ethyl alcohol (92.92 % by wt.) parts by vol.	Distilled water parts by vol.
I	100	0
II	80	20
III	60	40
IV	40	60
V	20	80

To prepare the charge for the still, four hundred ml. of the stock was measured out with a volumetric flask and the desired quantity of ester was added with a graduated pipette of one ml. capacity. The esters used in this work were of Eastman practical grade.

2. Distillation operation: The distillation of the samples was carried out according to the following steps:

Charging the still 400 ml. of the charge prepared as described above was introduced into the still. This was done by first removing the ground-to-fit joint stopper on the top of

the neck and pouring the liquid into the still through the vapor tube inside the neck by means of a small long stem funnel. Care was taken that no liquid was poured into the condenser. Before replacing the stopper a little neutral paraffin wax was applied to insure gas-tightness.

Heating the system Both the internal and external heaters were controlled by means of Variac transformers which regulated the power input by controlling the potential difference.

This system was so reliable that usually only a little adjustment was needed at the starting of the operation and after steady condition was reached no more adjustment was required.

Equilibrium After the heating started the reading of the thermometer would rise continuously. The equilibrium was indicated by a constant reading of the thermometer. The average time required to come to a steady state was about one hour. Two hours were allowed for the refluxing to insure positive equilibrium.

Pressure adjustment Since a pressure difference of less than 10 mm. of Hg would not change the equilibrium composition appreciably (11) no constant pressure device was used. All the determinations were made under atmospheric pressures between 752 to 758 mm. of Hg. An average of 755 was used for calculations.

Withdrawal of samples At the end of the refluxing, two Erlenmeyer flasks of 100 ml. capacity cooled in an ice bath were placed below the sampling cocks. The heating was stopped

immediately and both sampling cocks were opened at once to let the liquid and vapor condensate samples flow into the respective receivers. The receivers were well stoppered against evaporation of more volatile constituents. The time of sampling was kept at a minimum to reduce the change of composition of the liquids during sampling.

3. Determination of ethyl alcohol content: Ethyl alcohol was determined by the Pycnometric Method. The pycnometer used was of 10 ml. capacity provided with thermometer set into a ground-glass stopper. Compositions corresponding to the observed specific gravities were determined from the standard specific gravity tables (13) (14). No correction was made for the small quantities of esters present in the samples.

4. Determinations of esters: The ester content of the samples was determined by the standard saponification method (15). Owing to the size limitation of the condensate chamber of this still (20 ml.), duplicate samples of ten and five ml. volumes respectively were used for the vapor phase. For the residual liquid, samples ranging from 20 to 100 ml. according to their ester content were used. The saponification was effected by adding an excess of standard NaOH solution to the sample and aging for 24 hours at room temperature. The amount of alkali consumed by the ester was obtained by back titrating the excess NaOH with standard H_2SO_4 solution.

The data of this research given in Table III were treated according to the items as stated in the theoretical part of this report and their logical orders were followed.

The concentrations of ethyl alcohol expressed as percentage by weight in the ternary vapors and liquids of each of the five charge dilutions, calculated from specific gravity data, were listed in Table I; whereby a comparison with standard literature values obtained from binary mixture of ethyl alcohol and water could be made to show that the effect of small amount of ester on its volatility was negligible. The using of a standard y^*/x ratio, independent of the presence of ester was proved to be justified. The values of y^*/x for ethyl alcohol calculated from y^* and x values based on the data of Cornell and Montanna (7) are listed in Table II for use in the calculation of relative volatility of esters with respect to ethyl alcohol.

The concentrations of the esters in equilibrium vapors and residual liquids were calculated as grams per liter of liquid in the original data using C_l for liquid and C_v for vapor. To test the equilibrium constant derived from Henry's law in the theoretical part of the text, mol fractions should be used. But since the amount of ester was small, its mol quantity was negligible in comparison with the total number of mols. Hence for each alcohol water ratio the total number of mols of the liquid as well as that of the vapor phase were practically constant. Therefore the ratio C_v/C_l was directly proportional

TABLE I Specific Gravity of Equilibrium Vapor and Liquid

Concentration No.	Vapor Phase		Liquid Phase	
	Sp. Gr. 25°C.(1)	Eth. Alc. wt. % (2)	Sp. Gr. 25°C.(1)	Eth. Alc. wt. % (2)
I	0.80576	92.90	0.80975	92.10
II	0.83209	82.82	0.95984	71.48
III	0.83941	79.91	0.90812	50.77
IV	0.86817	68.00	0.96116	23.55
V	0.89067	58.41	0.97555	13.40

TABLE II y^*/x for Ethyl Alcohol

Concentration No.	Boiling Pt. °C.(3)	y^* (4)	x (4)	y^*/x
I	78.3	0.837	0.820	1.021
II	81.0	0.654	0.495	1.321
III	81.9	0.566	0.287	1.972
IV	68.0	0.543	0.108	4.195
V	69.5	0.355	0.057	6.228

Where y^* = Mol fraction in vapor phase at equilibrium

x = Mol fraction in liquid phase at equilibrium

- (1) Experimentally determined values
- (2) Obtained from standard tables
- (3) Obtained from Fig. 12 (17)
- (4) Calculated from wt. % in Table I

TABLE III Equilibrium Concentrations of Esters

Run No.	Alc. conc. mol %	Name of esters	C_v (1)	C_l (1)	C_v/C_l	y^*/x (2) (ave. val.)
1	82.00	Iso-amyl formate	4.68	4.14	1.13	
2	82.00	"	9.38	7.95	1.18	1.18
3	82.00	"	2.40	2.06	1.16	
4	49.50	"	7.30	3.54	2.06	
13	49.50	"	15.50	8.15	1.91	2.31
22	49.50	"	16.82	8.50	1.98	
5	28.70	"	16.82	3.64	4.62	
14	28.70	"	32.23	7.06	4.57	6.52
6	10.80	"	27.21	2.18	12.50	
15	10.80	"	48.00	3.72	12.90	19.78
7	5.70	"	24.20	0.61	39.70	64.66
16	82.00	Ethyl iso-valerate	5.24	8.70	0.61	
17	82.00	"	2.74	4.34	0.63	0.62
9	49.50	"	6.16	4.63	1.33	
18	49.50	"	11.99	8.55	1.40	1.64
19	28.70	"	13.80	3.62	3.81	
20	28.70	"	7.08	1.89	3.74	6.57
21	10.80	"	67.50	4.02	16.80	
23	10.80	"	34.02	2.15	16.15	27.00
12	5.70	"	26.80	0.47	57.00	80.00
24	82.00	Iso-propyl acetate	13.15	7.30	1.80	
25	82.00	"	6.65	3.65	1.83	1.82

TABLE III (continued)

Run No.	Alc. conc. mol %	Name of esters	C_V (1)	C_L (1)	C_V/C_L	$y^*/x(2)$ (ave.val.)
26	49.50	Iso-propyl acetate	19.90	8.86	2.25	2.54
27	28.70	"	32.60	6.06	5.27	7.77
28	10.00	"	61.60	4.02	15.35	
29	10.80	"	30.42	1.98	15.80	25.80
30	5.70	"	66.70	1.41	47.25	76.80
32	82.00	Iso-butyl formate	14.40	7.42	1.95	
44	82.00	"	7.38	3.69	2.00	1.021
33	49.50	"	23.00	7.18	3.28	1.321
34	28.70	"	30.60	6.14	4.97	1.972
35	10.00	"	52.20	4.67	11.42	4.195
36	5.70	"	30.40	1.28	23.70	
43	5.70	"	29.62	1.26	23.50	6.228
37	82.00	Ethyl iso-butyrate	8.90	7.90	1.12	
45	82.00	"	4.43	4.02	1.10	1.15
38	49.50	"	16.20	7.60	2.13	2.51
39	28.70	"	33.80	6.61	5.14	
46	28.70	"	17.20	3.31	5.20	7.31
40	10.80	"	52.20	2.72	19.15	33.00
41	5.70	"	53.30	0.746	71.31	
42	5.70	"	49.40	0.686	72.00	120.70

Where (1) Experimentally determined values.

(2) Calculated values.

FIG. 3.- C_v vs. C_1 CURVE

to the equilibrium constant. To save conversion of units, the ratios of C_v/C_l were listed in Table III, and a plot of C_v/C_l for different ester concentrations was prepared in Figure 3. The validity of Henry's law for this case can be verified readily from this results.

To calculate the relative volatility of esters with respect to ethyl alcohol by using equation V derived in the theoretical part, the C_v/C_l ratios were converted into y^*/x as shown in the sample calculations. In order to get better relative volatility curves as well as to ease the interpolation when using the data, smoothed curves of y^*/x for alcohol and y^*/x for esters based on the experimental values were prepared as in Figures 4, 5 and 6. From these curves at even intervals, alcohol concentrations were read off as listed in Tables IV to VIII and from these smoothed values of equilibrium constants, the corresponding relative volatilities were calculated and listed in the same tables. A plot of α versus alcohol concentration was prepared in Figures 7 and 8. The correction factor γ of Raoult's law defined in the theoretical discussion was calculated from the y^*/x ratio for each ester and their vapor pressure data appearing in the literature (16). The detailed calculations are shown by the sample calculations and the values of γ for esters at different concentrations of mixtures are listed in Tables IX to XIII. A plot of γ versus mol % of ethyl alcohol in solution is shown in Figure 9.

TABLE IV Smoothed Values of Equilibrium Constants
and Relative Volatilities

Ethyl Alcohol - Iso-propyl Acetate - Water System

Alcohol mol frac.	y^*/x for alcohol	y^*/x for ester	α
0.06	6.00	76.00	12.67
0.10	4.45	29.00	6.51
0.20	2.61	12.70	4.87
0.30	1.90	7.30	3.84
0.40	1.53	4.30	2.85
0.50	1.32	2.80	2.12
0.60	1.20	2.30	1.92
0.70	1.12	2.00	1.78
0.80	1.04	1.80	1.73

TABLE V Smoothed Values of Equilibrium Constants
and Relative Volatilities

Ethyl Alcohol - Iso-butyl Formate - Water System

Alcohol mol frac.	y^*/x for alcohol	y^*/x for ester	α
0.06	6.00	38.00	6.34
0.10	4.45	21.00	4.72
0.20	2.61	10.00	3.83
0.30	1.90	6.75	3.55
0.40	1.53	5.00	3.27
0.50	1.32	3.77	2.88
0.60	1.20	3.25	2.71
0.70	1.12	2.65	2.36
0.80	1.04	2.15	2.07

TABLE VI Smoothed Values of Equilibrium Constants
and Relative Volatilities

Ethyl Alcohol - Ethyl Iso-butyrate - Water System

Alcohol mol frac.	y^*/x for alcohol	y^*/x for ester	α
0.06	6.00	115.00	19.15
0.10	4.45	49.00	11.00
0.20	2.61	12.70	4.87
0.30	1.90	6.70	3.53
0.40	1.53	3.70	2.42
0.50	1.32	2.40	1.83
0.60	1.20	1.90	1.58
0.70	1.12	1.50	1.34
0.80	1.04	1.10	1.06

TABLE VII Smoothed Values of Equilibrium Constants
and Relative Volatilities

Ethyl Alcohol - Iso-amyl Formate - Water System

Alcohol mol frac.	y^*/x for alcohol	y^*/x for ester	α
0.06	6.00	63.00	10.50
0.10	4.45	21.90	4.92
0.20	2.61	10.70	4.10
0.30	1.90	6.10	3.21
0.40	1.53	3.70	2.42
0.50	1.32	2.40	1.82
0.60	1.20	2.00	1.67
0.70	1.12	1.70	1.52
0.80	1.04	1.30	1.25

TABLE VIII Smoothed Values of Equilibrium Constants
and Relative Volatilities

Ethyl Alcohol - Ethyl Iso-valerate - Water System

Alcohol mol frac.	y^*/x for alcohol	y^*/x for ester	α
0.06	6.00	73.00	12.31
0.10	4.45	29.50	6.63
0.20	2.61	12.10	4.64
0.30	1.90	5.90	3.11
0.40	1.53	3.00	1.96
0.50	1.32	1.50	1.15
0.60	1.20	1.10	0.92
0.70	1.12	0.90	0.80
0.80	1.04	0.70	0.67

FIG. 4.- EQUILIBRIUM CONSTANT CURVE OF ETHYL ALCOHOL (8)

FIG. 5.- EQUILIBRIUM CONSTANT OF ESTERS.

FIG. 6.- EQUILIBRIUM CONSTANT OF ESTERS

FIG. 7.- RELATIVE VOLATILITY CURVE OF ESTERS
(Smoothed Values)

FIG. 8.- RELATIVE VOLATILITY CURVE OF ESTERS
(Smoothed Values)

TABLE IX Raoult's Law Correction Factor
for Iso-propyl Acetate

Ethyl alc. in liquid mol frac.	y^*/x for ester (ave. val.)	B. Pt. of mixture °C.	Total pressure mm. Hg	Vapor press. of pure ester at B.P. of mixture mm. Hg	Correc. factor γ
0.820	1.82	78.3	755	482	2.85
0.495	2.54	80.1	755	506	3.78
0.287	7.77	81.9	755	525	11.20
0.108	25.80	86.0	755	570	34.20
0.057	76.80	89.5	755	605	95.80

TABLE X Raoult's Law Correction Factor
for Iso-butyl Formate

Ethyl alc. in liquid mol frac.	y^*/x for ester (ave. val.)	B. Pt. of mixture °C.	Total pressure mm. Hg	Vapor press. of pure ester at B.P. of mixture mm. Hg	Correc. factor γ
0.820	1.97	78.3	755	386	3.85
0.495	3.84	80.1	755	411	7.05
0.287	7.16	81.9	755	430	12.56
0.108	18.76	86.0	755	475	29.65
0.075	38.51	89.5	755	515	56.50

TABLE XI Raoult's Law Correction Factor
for Ethyl Iso-butyrate

Ethyl alc. in liquid mol frac.	y^*/x for ester (ave. val.)	B. Pt. of mixture °C.	Total pressure mm. Hg	Vapor press. of pure ester at B.P. of mixture mm. Hg	Correc. factor γ
0.820	1.15	78.3	755	271	3.20
0.495	2.51	80.1	755	293	6.46
0.287	7.31	81.9	755	310	17.80
0.108	33.00	86.0	755	350	71.15
0.057	120.70	89.5	755	391	233.30

TABLE XII Raoult's Law Correction Factor
for Iso-amyl Formate

Ethyl alc. in liquid mol frac.	y^*/x for ester (ave. val.)	B. Pt. of mixture °C.	Total pressure mm. Hg	Vapor press. of pure ester at B.P. of mixture mm. Hg	Correc. factor γ
0.820	1.18	78.3	755	166	5.36
0.495	2.31	80.1	755	180	9.69
0.287	6.53	81.9	755	195	25.30
0.108	19.78	86.0	755	230	65.00
0.057	64.66	89.5	755	265	184.00

TABLE XIII Raoult's Law Correction Factor
for Ethyl Iso-valerate

Ethyl alc. in liquid mol frac.	y^*/x for ester (ave val.)	B. Pt. of mixture °C.	Total pressure mm. Hg	Vapor press. of pure ester at B.P. of mixture mm. Hg	Correc. factor γ
0.820	0.62	78.3	755	112	4.17
0.495	1.64	80.1	755	122	10.15
0.287	6.57	81.9	755	130	38.20
0.108	27.00	86.0	755	153	133.00
0.057	80.00	89.5	755	175	345.00

FIG. 9.- RAOULT'S LAW CORRECTION FACTOR CURVE.

DISCUSSION

The equilibrium compositions of ethyl alcohol-water mixtures containing small amounts of ester listed in Table I can be compared with the accepted values of Cornell and Montanna of Table XVI. It is found that they are very close and therefore it can be safely assumed that the presence of small amount of ester (below one per cent) does not alter the compositions appreciably. The standard value of y^*/x can be used for the relative volatility calculation of the present work.

From Table III and Figure 3 it was seen that for each concentration of ethyl alcohol in solution the C_V/C_1 ratio were constant independent of the ester concentrations. This was in agreement with Henry's law which is valid for small quantity of volatile solutes dissolved in solvents. Based on this fact and equation V derived in the theoretical part, it could be inferred that for a certain alcohol concentration, the relative volatility of esters would be also remaining constant as long as the concentration limit for Henry's law was not exceeded.

As the alcohol concentration varied the y^*/x ratios for esters changed greatly. This could be seen from the results contained in Tables III to VIII. Examining iso-propyl acetate in Table III, it is noted that at an alcohol concentration of 82.0 per cent the y^*/x ratio for ester is 1.12 while for an alcohol concentration of 5.7 percent the y^*/x ratio is 76.00. This change is apparently caused by the nature and especially

the boiling points of the mixtures changed with the alcohol concentrations. In order to follow the tendency of this change the correction factor of Raoult's law were calculated, listed in Tables IX to XIII and plotted in Figure 9. The values became surprisingly large in the more dilute region. This was probably because all these esters were completely miscible with ethyl alcohol but slightly soluble in water. When the alcohol concentration was high, the esters were kept in solution by the influence of alcohol. When the amount of water predominated, being slightly soluble, the esters tended to escape. Therefore although some esters have higher boiling points than that of both alcohol and water, they can be much more volatile.

The calculated results of relative volatilities of the five esters given in Tables IV to VIII could be of direct use by themselves in the design calculations. However some correlations between either the relative volatilities or the equilibrium constants and the physical constants such as molecular weight, boiling point and so on would be highly desirable. After some trials it was found that no simple quantitative relationship could be established except for the range of alcohol concentration of more than 50 mol per cent. Within this range the increase of relative volatilities were inversely proportional to the alcohol concentrations. For alcohol concentrations of less than 50 per cent the relative volatilities increased rapidly as the alcohol decreased.

SUMMARY AND CONCLUSIONS

1. The vapor-liquid equilibrium constants of five esters in different mixtures of ethyl alcohol and water were determined experimentally with the Othmer recycling still. The esters were iso-propyl acetate, iso-butyl formate, ethyl iso-valerate, ethyl iso-butyrate, and iso-amyl formate.
2. The relative volatilities of the five esters with respect to ethyl alcohol were calculated from the equilibrium constants for esters and the corresponding equilibrium constants of ethyl alcohol of different concentrations.
3. The equilibrium constants and the relative volatilities could be used directly for the calculation of columns in alcohol purification.
4. Although the equilibrium constants were in agreement with Henry's law for small concentrations of ester in solution the volatility of esters in these mixtures were highly abnormal. Correction factors of Raoult's law for some cases rose higher than three hundred. No way available at present seems to be better than a quick, accurate experimental method for the obtaining of these equilibrium constants.
5. The relative volatilities of esters were far greater in the low alcohol mixtures.

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APPENDIX

LIST OF SYMBOLS

C_v	Concentration in vapor, gm./1000 ml.
C_l	Concentration in liquid, gm./1000 ml.
K	Defined on page 5
K'	Purification coefficient of Barbet
K''	Henry's law constant
K^*	Equilibrium constant
k'	Defined on page 5
p	Partial pressure
P_T	Total pressure
P_0	Vapor pressure of pure substance
x	Mol fraction in liquid
y	Mol fraction in vapor
y^*	Mol fraction in equilibrium vapor
α	Relative volatility
γ	Correction factor of Raoult's law

SAMPLE CALCULATIONS

Conversion of C_v/C_l to y^*/x for esters:

Run No. 24, iso-propyl acetate, molecular weight 102,
specific gravity 0.877

$C_v = 13.15$ gm. per 1000 ml. vapor

$C_l = 7.3$ gm. per 1000 ml. liquid

Number of mols in vapor $= 13.15/102 = 0.129$

Number of mols in liquid $= 7.3/102 = 0.072$

Volume of alcohol and water in vapor

$$= 1000 - 13.15/0.877 = 985.0 \text{ ml.}$$

Volume of alcohol and water in liquid

$$= 1000 - 7.3/0.877 = 991.7 \text{ ml.}$$

From Table XIV, total number of mols of alcohol and water
in 100 gms. of vapor is 2.411 at sp. gr. of 0.80576.

Total number of mols of alcohol and water in 100 gms. of
liquid is 2.438 at sp. gr. of 0.80975.

In 985.0 ml., the Number of mols of alcohol and water

$$= (985)(0.80576)(2.411/100)$$

$$= 19.136$$

Total number of mols of alcohol and water and ester in one
liter of vapor

$$= 19.136 + 0.129 = 19.265$$

In 991.7 ml. of liquid, the number of mols of alcohol and
water

$$= (991.7)(0.80975)(2.438/100)$$

$$= 19.535$$

Total number of mols of alcohol, water and ester in one
 liter of liquid $= 19.535 + 0.072$
 $= 19.607$

Therefore $y^*/x = (0.129/0.072)(19.607/19.265)$
 $= 1.8234$

Correction factor for Raoult's law:

By equation $P_T y^* = \gamma (P_O)(x)$
 $\gamma = (y^*/x)(P_T/P_O)$

For run No. 24, $y^*/x = 1.823$, boiling point of mixture is
 78.3°C. , vapor pressure of pure iso-propyl
 acetate is 482 mm. Hg (from Fig. 10), and
 total pressure is 755 mm. Hg.

Therefore $\gamma = (1.823)(755/482) = 2.85$

TABLE AIV Equilibrium Compositions of Alcohol-Water Mixtures

Conc. No.	Ethyl alc. % wt.	Water % wt.	Ethyl alc. No. of mols	Water No. of mols	Total No. of mols per 100 gm.	Ethyl alc. mol frac.	Water mol frac.
LIQUID PHASE							
1	92.10	7.90	2.000	0.438	2.438	0.820	0.180
2	71.49	28.52	1.552	1.583	3.135	0.495	0.505
3	50.77	49.23	1.102	2.732	3.834	0.287	0.713
4	23.55	76.45	0.511	4.242	4.753	0.108	0.892
5	13.40	86.60	0.291	4.806	5.097	0.057	0.943
VAPOR PHASE							
1	92.90	7.10	2.017	0.394	2.411	0.837	0.163
2	82.82	17.18	1.798	0.953	2.751	0.654	0.346
3	76.91	23.09	1.670	1.281	2.951	0.566	0.434
4	60.00	39.00	1.476	1.776	3.252	0.453	0.546
5	58.41	41.59	1.268	2.308	3.576	0.355	0.645

TABLE XV Physical Constants of Esters (14)

Name	Molecular weight	Boiling point	Density
Ethyl iso-valerate	130.16	135.0°C.	0.866 (20/4)
Iso-amyl formate	116.16	123.5 "	0.871 (20/4)
Ethyl iso-butyrate	116.16	111.7 "	0.869 (20/4)
Iso-butyl formate	102.13	99.2 "	0.875 (20/4)
Iso-propyl acetate	102.13	99.0 "	0.877 (16/4)
Ethyl alcohol	46.06	78.5 "	0.789 (20/4)
Water	18.02	100.0 "	1.000 (4/4)

TABLE XVI Ethyl Alcohol, Water, Equilibrium Data
Cornell and Montanna

Ethyl alcohol in liquid		Ethyl alcohol in vapor	
wt. %	mol fraction	wt. %	mol fraction
0.60	0.003	6.20	0.025
1.10	0.005	10.90	0.046
2.00	0.008	20.00	0.089
2.10	0.009	19.90	0.088
3.00	0.012	26.20	0.122
3.40	0.014	29.00	0.138
4.90	0.020	37.40	0.190
6.15	0.025	42.30	0.223
6.80	0.028	44.80	0.241
8.50	0.035	49.30	0.275
10.14	0.042	53.10	0.307
13.60	0.058	58.90	0.295
15.14	0.065	61.10	0.380
17.14	0.075	63.00	0.400
19.04	0.084	64.70	0.417
20.90	0.094	66.30	0.435
22.70	0.103	67.80	0.451
25.35	0.117	69.10	0.466
26.85	0.126	69.70	0.473
29.90	0.143	71.30	0.493
32.95	0.161	72.30	0.505

TABLE XVI (continued)

Ethyl alcohol in liquid		Ethyl alcohol in vapor	
wt. %	mol fraction	wt. %	mol fraction
33.30	0.163	72.90	0.512
35.60	0.184	73.70	0.523
38.00	0.194	74.00	0.527
41.24	0.215	74.80	0.537
45.10	0.234	75.90	0.552
48.90	0.272	76.80	0.564
53.00	0.305	77.60	0.576
57.30	0.341	78.70	0.590
61.30	0.382	79.90	0.608
65.60	0.429	80.90	0.623
68.60	0.460	81.70	0.636
70.90	0.488	82.60	0.650
74.80	0.537	83.90	0.671
78.00	0.581	85.00	0.690
81.50	0.623	86.50	0.715
83.90	0.672	87.70	0.735
86.00	0.706	88.80	0.756
88.00	0.741	90.00	0.778
90.10	0.780	91.30	0.803
92.80	0.834	93.30	0.844
94.20	0.864	94.31	0.866
96.28	0.910	96.16	0.907
98.07	0.952	97.88	0.948

TABLE XVII Vapor Pressure of Esters (16)

Vapor pressure mm. Hg	Esters				
	A*	B*	C*	D*	E*
Temperature °C.					
1	-30.3	-32.7	-24.3	-17.5	-6.1
5	-17.4	-11.4	-2.4	5.4	17.0
10	-7.2	-0.8	6.4	17.1	28.7
20	4.2	11.0	20.6	30.0	41.3
40	17.0	24.1	35.8	44.0	55.2
60	25.1	32.4	42.3	53.3	64.0
100	35.7	43.4	53.5	65.4	75.9
200	51.7	60.0	71.0	83.2	93.8
400	69.8	79.0	90.0	102.7	114.0
600	89.0	98.2	110.1	123.3	134.3

* A Iso-propyl acetate

B Iso-butyl formate

C Ethyl iso-butyrate

D Iso-amyl formate

E Ethyl iso-valerate

FIG. 10.- VAPOR PRESSURE CURVE OF ESTERS(16)

FIG. 11.- ETHYL ALCOHOL-WATER EQUILIBRIUM
CURVE (8), (760m.m. Hg)

FIG. 12.- BOILING POINT CURVE OF ETHYL ALCOHOL-WATER MIXTURE (17)

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VITA

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