Vapor Pressure and Vapor-Liquid Equilibrium Data for Methyl Esters of the Common Saturated Normal Fatty Acids

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NEW vapor pressure-temperature data are given in the form of Antoine equation constants for methyl esters of the normal saturated fatty acids having 6, 8, 10, 12, 14, 16, and 18 carbon atoms in the range between 20 and 200 mm. of Hg absolute pressure. Similar data are given for 1-hexanol. Also given are boiling point-composition data and directly measured vapor-liquid composition equilibrium data over similar pressure ranges for the binary mixtures of methyl esters with 6-8, 8-10, 10-12, 12-14, 14-16, and 16-18 carbon atoms in the parent acid chain, and for the system 1-hexanol-1-octanol. The systems are ideal with relative volatilities at 30 mm. of Hg absolute pressure ranging from approximately 4.8 to 5.8 over the composition range 0.1 to 0.9 mole fraction methyl caproate in the methyl caproate-methyl caprylate binary; for the same pressure and range in composition the relative volatilities varied from approximately 2.3 to 2.4 for the methyl palmitate-methyl stearate system. The relative volatilities decrease as the molecular weight increases and decrease with increasing pressure. Equilibrium data are in close agreement with values predicted with the use of Raoult's and Dalton's laws, but careful experimental work is necessary with such systems at these pressures and temperatures to avoid incorrect values for the directly measured equilibrium data and erroneous vapor pressure–temperature data.

The first experimental vapor-liquid equilibrium work in this laboratory on these systems gave erroneous (low) vapor composition values in spite of all normal precautions; these values were not thermodynamically consistent. The new experimental vapor pressure measurements were made to resolve inconsistencies in similar data in the literature and to aid in resolving the thermodynamic inconsistencies in the vapor-liquid equilibrium data for the binary mixtures of the substances under study. For the latter purpose it was convenient to obtain vapor pressure–temperature in the same apparatus in which subsequent temperature and composition equilibrium measurements would be made, since any systematic error in pressure or temperature measurement incurred while obtaining vapor pressure data should also occur during equilibrium measurements in the same apparatus. As a result, the errors should at least partly compensate, whereas if the two types of measurements were made in different pieces of apparatus, the errors could be cumulative, and extensive calibration of apparatus would be necessary.

The determination of the entire set of data as a unit, and the use of correlations for the homologous series as well as the usual correlations for data on binary and individual compounds, strengthened the entire set of data, and provide a basis for prediction of properties for other similar compounds or similarly related groups.

This article also gives empirical and semitheoretical equations and procedures for correlating vapor pressure data for the compounds in a homologous series, and decribes how the methods may be used to predict data for compounds for which limited or no measurements are available. Also included is a correlation of the relative volatilities of binary mixtures of members of a homologous series as a function of the molecular weight. Supplementary data such as predicted vapor-liquid equilibrium values, additional examples for the various correlations as well as other correlations, vapor pressure–temperature values calculated from the Antoine constants, comparison of these with literature values from several sources, and a more detailed description of experimental methods are available (*22*).

EXPERIMENTAL

Apparatus. Experimental measurements were made in a recirculating still incorporating a Cottrell tube with enlargements as described by Papahronis (*15*) and illustrated in Figure 1. Temperatures were measured by a copper-constantan thermocouple and a Leeds and Northrup Type K-3 potentiometer. The thermocouple was calibrated at the ice point, steam point, and freezing points of tin and lead samples from the National Bureau of Standards. Temperatures measured with this couple were considered to be accurate to within 0.2° C. (*24*).

A cathetometer which could be read to within 0.05 mm. was used to read the pressure indicated by a mercury manometer. This pressure was corrected to 0° C. to allow for thermal expansion of mercury at higher temperatures. No correction was made for the linear expansion of the steel cathetometer scale, since it was calibrated at 25° C. and any corrections involved would have been negligible.

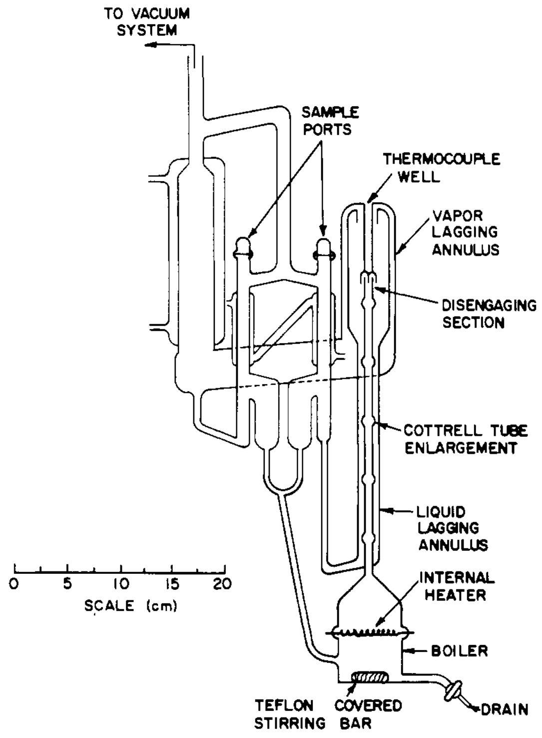

Figure 1. Papahronis still

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Procedure. The procedure followed was essentially the same as that described by Papahronis (*15*). In addition, the disengaging section of the still was wrapped with electrical heating tape to provide better control of heat losses when operating at elevated temperatures. After steady Cottrel action was obtained, the heat supply was regulated to keep the outer wall of the disengaging section 2 to 5° C. below the equilibrium temperature. Condensation of vapors in the annulus maintained adiabatic conditions within the disengaging chamber.

VAPOR PRESSURE–TEMPERATURE DATA

Experimental vapor pressure–temperature data are recorded in Table I. These were fitted to the Antoine equation using a digital computer in a procedure described by Rose and others (*18*). Antoine constants are given in Table II; calculated vapor pressure–temperature values have been tabulated elsewhere (*22*).

Correlation and Prediction. Various methods of correlation have been proposed and applied to many systems. In general these methods may be divided into two categories: (1) The complete vapor pressure curve is predicted from one or more directly measured points on the curve and in some cases from additional data such as critical properties or other physical properties (*4, 7, 10, 11, 13, 16, 17, 21*). (2) When no vapor pressure data for a particular substance are available, predictions are made using auxiliary data such as vapor pressures of a reference substance, densities, viscosities, etc. (*2, 5, 8, 12, 14, 16, 17, 23*).

Most of the methods cited were in general either inaccurate when applied to the methyl esters of the normal saturated fatty acids, or the required auxiliary data were not available. Among the methods involving only one or two points on the vapor pressure–temperature curve Brown (*4*) described a procedure for liquids obeying Hildebrand's rule. With tables supplied in the reference and one point on the curve, the method allows prediction of the entire vapor pressure curve. When applied to methyl caproate, the pressure predicted for a temperature of 90.3° C. was 92.6 mm. of Hg, while the experimental value was 100 mm. of Hg.

Ogata and Tsuchida (*12*) have developed and expression for the boiling point as a function of the latent heat of vaporization. According to their data, the relationship should be linear for the methyl esters of the normal saturated fatty acids, but the values calculated from the present vapor pressure data do not substantiate this.

Other methods which required only one point on the vapor pressure curve gave no better results, except that of Myers and Fenske (*11*). This method as originally presented was based upon hydrocarbon vapor pressure data but has been successfully applied in the present work to the methyl, ethyl, and butyl esters of the normal saturated fatty acids. The procedure is illustrated as follows, the objective being prediction of vapor pressure–temperature values for methyl caproate. The boiling points at 50 mm. of Hg of each of the esters are plotted on an arithmetic scale against the respective boiling points at another pressure, as in Figure 2. The procedure of plotting the boiling points at 50 mm. of Hg. vs. the boiling points at another pressure is repeated until a number of pressure parameters are obtained. From this chart predictions are made as follows. If the boiling point of methyl caproate at 20 mm. of Hg is known to be 54.7° C., the intersection of the 20 mm. line with this temperature is located. Proceeding horizontally from this point, the intersection with other constant pressure lines determines the temperatures at the respective pressures. At 100 mm. of Hg the predicted and experimental temperatures are both 90.3° C.

This method proved to be especially valuable in that the chart constructed from data for the methyl esters was

Table I. Experimental Vapor Pressure Data

Pressure, Mm. Hg	Temp., ° C.	Pressure, Mm. Hg	Temp., ° C.	Pressure, Mm. Hg	Temp., ° C.
Methyl Caproate		Methyl Caprylate		Methyl Caprate	
11.8	44.5	32.7	100.3	10.8	107.3
20.8	55.7	40.8	105.5	14.5	114.1
26.2	60.3	49.0	109.8	17.4	118.2
31.7	64.2	59.9	114.7	21.5	122.8
39.8	69.0	60.8	115.0	25.1	126.5
49.7	73.8	69.6	118.5	27.8	128.8
54.4	75.9	74.8	120.3	29.9	130.6
58.9	77.6	77.0	121.0	39.3	137.3
69.7	81.5	86.3	124.0	47.3	142.0
80.3	84.9	96.1	126.9	59.7	147.8
93.1	88.5	100.7	128.1	61.4	148.6
115.6	93.9	101.6	128.4	67.4	151.1
144.0	99.6	102.5	128.6	77.9	155.0
154.0	101.3	102.6	128.6	81.1	156.2
174.8	104.8	105.5	129.4	89.0	158.8
		112.5	131.1	100.1	162.2
		113.8	131.5	100.1	162.2
		113.9	131.4	107.6	164.2
Methyl Laurate		114.2	131.5	108.0	164.3
		130.5	135.1	118.4	167.1
27.4	157.8	141.4	137.3	126.3	169.0
40.1	167.4	142.6	137.6	150.9	174.3
53.1	174.8	148.0	138.8	168.7	177.8
59.1	177.8	159.6	141.0	188.7	181.4
66.4	181.1	186.5	145.7	209.1	184.7
74.2	184.0			232.2	188.2
82.7	187.4	Methyl Palmitate			
93.4	191.0				
103.7	194.2	14.3	193.6		
117.9	198.1	16.9	194.7		
144.4	204.5	23.2	204.6		
160.7	208.1	26.9	208.6		
182.2	212.3	33.9	214.8		
		40.0	219.5	Methyl Myristate	
		44.9	222.9		
		48.6	225.1	13.0	166.0
1-Hexanol		52.7	227.3	15.9	171.1
		57.5	229.9	22.2	179.2
10.3	60.9	62.2	235.8	22.7	179.6
12.9	64.7	69.7	232.5	27.9	185.0
16.7	69.2			36.9	192.3
19.4	71.9	Methyl Stearate		44.0	197.1
21.6	73.7			53.9	202.9
32.0	80.8	9.5	204.1	62.8	207.3
41.1	85.6	10.2	205.8	70.0	210.5
44.8	87.2	11.1	208.4	80.3	214.7
56.1	91.6	12.9	212.1	98.7	218.8
61.3	93.5	15.3	216.6	100.4	221.6
69.1	95.9	19.0	222.3	114.1	225.6
76.0	97.9	23.1	227.3	123.1	228.0
88.0	101.0	25.1	229.4	133.0	230.6
95.9	102.8	26.0	230.7	150.8	234.7
112.1	106.3	31.7	237.9	165.2	237.8
124.0	108.5	36.2	239.7		

Table II. Antoine Equation Constants

$\log_{10} P = A - B/(t + C)$ where P = absolute pressure, mm. of Hg and t = temperature, ° C.

Compound	*A*	*B*	*C*
Methyl caproate	7.82872	1935.119	241.704
Methyl caprylate	7.57031	1920.100	216.780
Methyl caprate	7.56403	2046.483	205.635
Methyl laurate	6.78282	1600.662	141.648
Methyl myristate	7.43265	2136.760	171.966
Methyl palmitate	7.17574	2017.660	142.557
Methyl stearate	5.42311	1023.847	25.048
1-hexanol	8.51907	2118.22	221.181

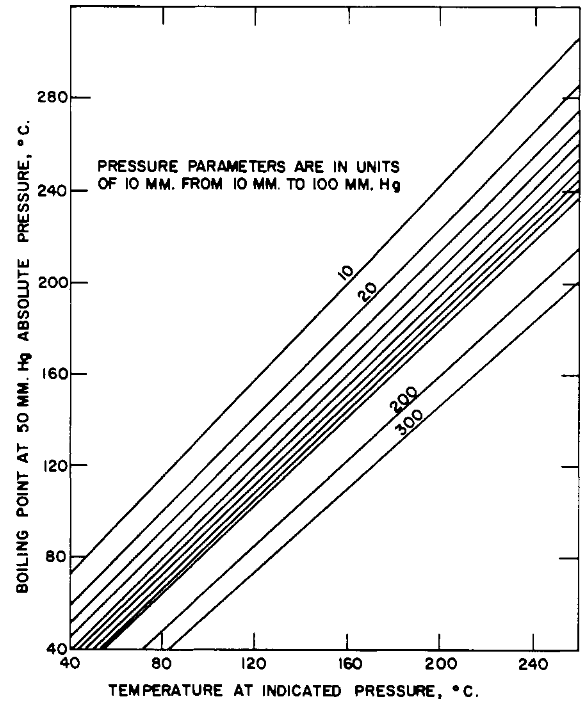

Figure 2. Myers-Fenske vapor pressure correlation applied to methyl esters of saturated normal fatty acids from 10 to 300 mm. of Hg absolute pressure

Table III. Comparison of Vapor Pressure Data Predicted by Method of Myers and Fenske with Experimental Data of Liang for Ethyl Caprylate and Butyl Caprate[a]

Pressure, Mm. Hg	Temperature, ° C.			
	Ethyl Caprylate		Butyl Caprate	
	Exptl.	Predicted	Exptl.	Predicted
10	87.0	87.4	143.3	143.3
20	101.8	101.7	159.3	159.2
40	117.6	[b]	176.4	[b]
50	123.0	122.8	182.6	182.3
60	127.6	127.4	187.4	187.4
80	134.8	134.9	195.6	195.8
100	140.8	140.9	201.8	202.6

[a] Chart used in predictions was constructed using data obtained for methyl esters in the current work.

[b] Temperature at this pressure was used to predict data at other pressures.

accurate when used for predicting values for the ethyl and butyl esters using the data of Liang (*9*) for prediction and comparison. Values predicted for all the esters are compared with experimental data in Tables III and IV.

Of the procedures examined which use two points on the vapor pressure–temperature curve, the method of Othmer (*13*) proved to be the best. At a given temperature the vapor pressure of a substance is related to that of a reference compound

$$\text{Log } P' = A \text{ Log } P + B$$

where P' and P are the vapor pressures of the substance and reference compound respectively, and A and B are constants. For methyl caproate, predicted temperatures were within 0.1° C. (Table IV).

Prediction When No Data for Desired Substance Are Available. Various correlations between boiling points and molecular structure have been presented in the literature (*5, 14, 16, 17*). Most of these could not be used with the systems considered here since either the necessary auxiliary data were not available, or the methods proved to be unsatisfactory. A new method was devised which requires that similar data for other compounds in the same homologous series as the substance in question be available. In addition, the vapor pressure data of the homologous series of normal paraffins given by Camin, Rossini, and others (*6, 19, 25*) are used. This method was developed from the observation that the vapor pressure–temperature data for the 1-alkenes and ethyl esters of saturated normal fatty acids could be correlated as a function of boiling point differences and carbon number.

To predict the vapor pressure data for methyl caproate from the vapor pressures of methyl caprylate, methyl caprate, methyl laurate, and methyl myristate, the following procedure was followed. At a given pressure, the boiling temperatures of octane and methyl caprylate were determined, and the difference between them was calculated. This difference, ΔT, was then obtained for decane and methyl caprate, dodecane and methyl laurate, tetradecane and methyl myristate, and hexadecane and methyl palmitate (Table IV). The paraffin was then considered as the reference substance, and a plot of log ΔT vs. $(n)^{1/2}$ where n is the number of carbon atoms in the reference paraffin, was then constructed with different vapor pressures as the parameter (Figure 3). From the best straight line drawn through the points, the ΔT values corresponding to $n = 6$ were determined. These ΔT values represented the temperature differences between methyl caproate and hexane at the respective pressures, and

Table IV. Differences between Boiling Points of Methyl Esters of Saturated Normal Fatty Acids and Vapor Pressure–Temperature Data for Methyl Caproate

Pressure, Mm. Hg	Temperature Difference, ΔT							Vapor Pressure–Temperature Data ° C.			
	Exptl.						Predicted		Predicted[a]		
	C_8	C_{10}	C_{12}	C_{14}	C_{16}	C_6	C_6	Exptl.	(1)	(2)	(3)
10	56.3	48.4	43.4	39.1	35.0	66.8	66.0	41.7	40.9	41.7	41.5
20	58.0	49.5	44.3	39.5	35.8	69.0	68.3	54.7	54.0		54.6
30	59.0	50.9	44.7	39.9	36.3	70.4	69.9	63.0	62.5	62.9	62.9
40	59.8	51.5	45.3	40.2	36.7	71.4	71.1	69.1	68.8	69.0	69.0
50	60.4	52.1	45.7	40.5	36.9	72.1	71.9	74.0	73.8	73.9	
60	60.9	52.5	46.0	40.8	37.1	72.7	72.4	78.1	77.8	78.1	78.1
70											81.7
80	61.6	53.1	46.4	41.3	37.5	73.8	73.2	84.9	84.3	84.8	85.0
90											87.8
100	62.2	53.6	47.0	41.7	37.7	74.5	74.1	90.3	89.9		90.4
200	64.0	55.0	48.3	43.3	38.5	76.8	76.5				

[a] (1) Predicted using paraffin vapor pressure data. (2) Othmer method. (3) Myers and Fenske method.

can be directly converted into the desired predicted temperature values for methyl caproate as shown in Table IV, column 1. Predictions for a primary alcohol are given in Table V and Figure 4.

VAPOR-LIQUID EQUILIBRIUM

Experimental vapor-liquid equilibrium data were obtained in the same still and with the same procedure which were used for vapor pressure measurements. Each of the binary systems was studied under isobaric conditions: pressures used were 20, 30, 40, 50, and 100 mm. of Hg absolute. Samples of liquid and vapor condensate were analyzed by refractive indices using a five-place Valentine refractometer or a six-place Brice-Phoenix differential refractometer (*3*) for mixtures with a small difference in refractive index between pure components.

The systems examined were methyl caproate-methyl caprylate, methyl caprylate-methyl caprate, methyl caprate-methyl laurate, methyl laurate-methyl myristate, methyl myristate-methyl palmitate, methyl palmitate-methyl stearate, and 1-hexanol-1-octanol. Experimental equilibrium data are listed in Table VI. Predicted values can be readily calculated from the Antoine equation constants for the respective components of a binary mixture.

All of the systems gave data agreeing closely with values predicted assuming the mixtures to be ideal, and the vapors to conform to Dalton's law. These predicted vapor-liquid equilibrium compositions and boiling point-composition values were obtained using only experimental vapor pressure data for the pure components. A typical comparison of experimental with predicted values is given in Figure 5, the conventional *x-y* diagram. The ideal results were expected, since Acciarri (*1*) and Papahronis (*15*) found the caproic-caprylic acid and the normal primary alcohol systems, respectively, to be ideal or nearly so. However, Sanders (*20*) using an earlier and less elaborate model of the apparatus with the methyl caproate-methyl caprylate system at 50 mm. of Hg absolute pressure obtained entirely different *x-y* data which were inconsistent with predicted values. Acciarri (*1*) showed that with fatty acid mixtures the directly measured vapor compositions were more nearly correct if the Cottrell tube of the apparatus was modified by filling it with packing material to give better contact between liquid and vapor. Papahronis found with the normal primary alcohols that the use of many expanded sections in the Cottrell tubes gave the same kind of results as packed Cottrell tubes. Use of this kind of apparatus with ester mixtures in the present work produced thermodynamically consistent data.

Prediction. It would be desirable to be able to predict

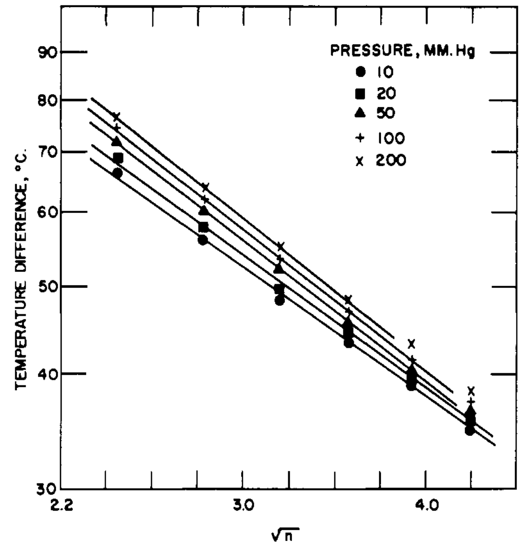

Figure 3. Logarithm of differences between boiling points of methyl esters of saturated *n*-fatty acids and corresponding paraffins vs. square root of number of carbon atoms in paraffins

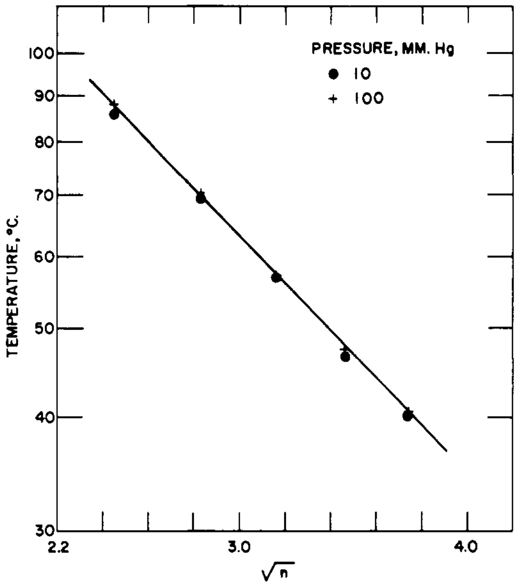

Figure 4. Logarithm of difference between boiling points of normal primary alcohols and corresponding paraffins vs. square root of number of carbon atoms in paraffins

Table V. Differences between Boiling Points of Normal Primary Alcohol and Corresponding Normal Paraffins; Vapor Pressure–Temperature Data for 1-Hexanol

Pressure, Mm. Hg	Temperature Difference, ΔT ° C.						Vapor Pressure–Temperature Data ° C.	
	Exptl.					Predicted		
	C_8	C_{10}	C_{12}	C_{14}	C_6	C_6	Exptl.	Predicted[a]
10	69.5	56.8	46.6	40.2	85.6	87.9	60.5	62.8
20	69.5	56.3	47.0	40.1	86.6	87.9	72.3	73.6
30	69.4	56.7	47.0	40.1	87.0	87.9	79.6	80.5
40	69.5	56.7	47.3	40.1	87.4	87.9	85.1	85.6
50	69.4	56.7	47.4	40.1	87.5	87.9	89.4	89.8
60	69.5	56.6	47.4	40.2	87.7	87.9	93.1	93.3
80	69.4	56.5	47.4	40.3	87.9	87.9	99.0	99.0
100	69.4	56.5	47.4	40.4	88.0	87.9	103.8	103.7
200	69.2	56.2	47.2		87.9	87.9	119.5	119.5
300	69.1	56.0	47.9		87.5	87.9	129.4	129.8

[a] Calculated from predicted ΔT.

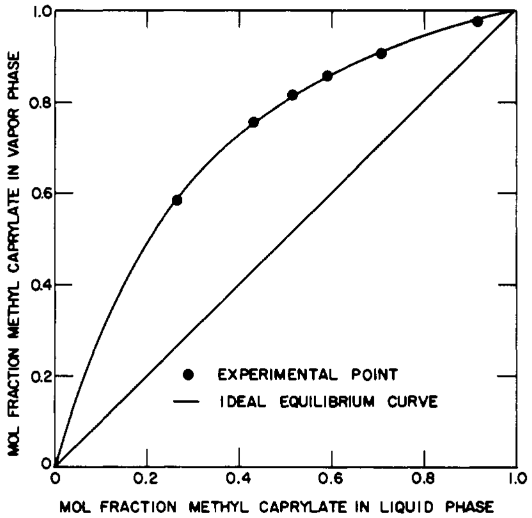

Figure 5. Vapor-liquid equilibrium diagram for methyl caprylate–methyl caprate mixtures at 30 mm. of Hg absolute pressure

equilibrium data for mixtures of a homologous series from a limited amount of data instead of measuring vapor pressure and equilibrium data for all the components as done for the methyl esters. A correlation had been developed relating the relative volatility of binary mixtures in a homologous series at constant pressure and constant liquid composition to a function of the chain length of the components involved. The relationship is not linear in all cases and therefore is more accurate when used by interpolation rather than by extrapolation for the prediction of data for systems for which none are available.

The method was developed by applying it first to binary mixtures of the normal paraffins, using the vapor pressure data of the pure components as given by Camin, Rossini, and others (*6, 19, 25*), and assuming that mixtures of pairs of these compounds would act ideally. From these data the relative volatility was determined at constant pressure and constant liquid composition for each binary mixture. The number of carbon atoms in the molecule of each of the two components was determined, and average, n_{av}, calculated. The logarithm of the relative volatility for each pair of compounds was plotted *vs.* the reciprocal of n_{av}, resulting in a nearly straight line with parameters for various pressures and liquid compositions (Figure 6).

When the method was applied to the fatty acid derivatives n_{av} was determined from the number of carbon atoms in the parent acid molecule. The lines obtained by plotting this $1/n_{av}$ *vs.* logarithm of relative volatility had appreciable curvature for the methyl esters and alcohols (Figure 7, 8). As a consequence this method is more useful and accurate for predictions involving interpolation with respect to n, than when extrapolation is necessary.

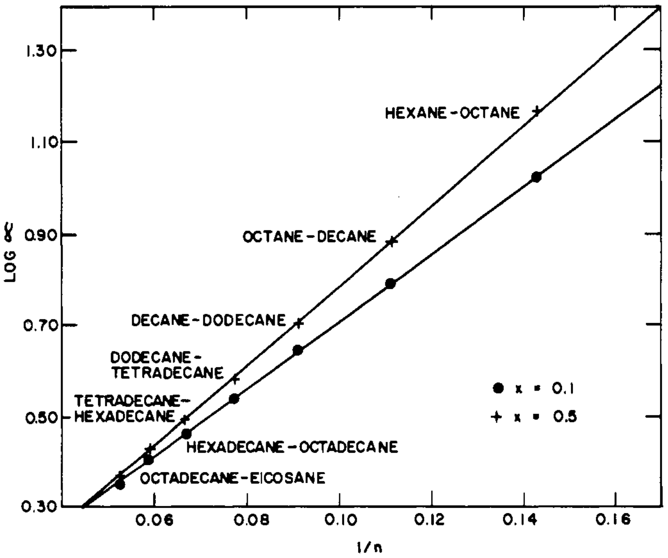

Figure 6. Logarithm of relative volatility *vs.* reciprocal of average carbon chain length *n*, for *n*-paraffins at 30 mm. of Hg absolute pressure and various liquid compositions

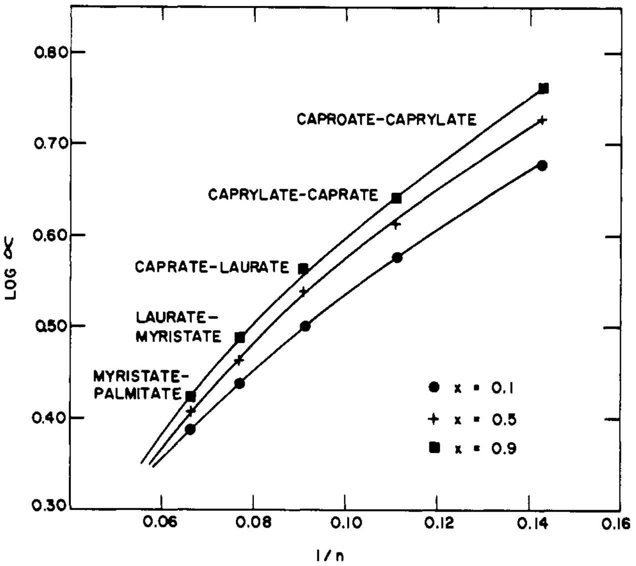

Figure 7. Logarithm of relative volatility *vs.* reciprocal of average carbon chain length, *n*, for methyl esters of saturated *n*-fatty acids at 30 mm. Hg. absolute pressure and various liquid compositions

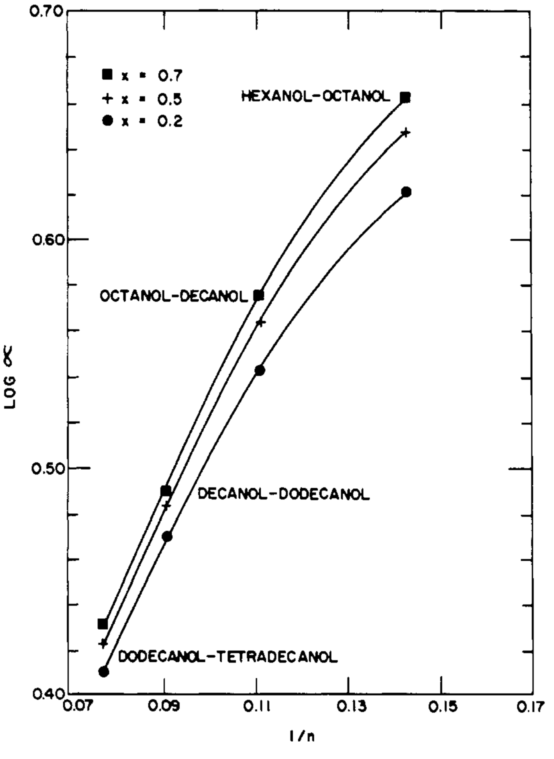

Figure 8. Logarithm of relative volatility, α *vs.* reciprocal of average carbon chain length, *n*, for normal primary alcohols at 50 mm. of Hg pressure at various liquid compositions

Table VI. Experimental Vapor-Liquid Equilibrium Data

x	y	Temp., ° C.	α	Corrected Pressure, Mm. Hg
Methyl Caproate–Methyl Caprylate				
Pressure 20 Mm.				
0.568	0.880	63.1	5.58	20.0
0.615	0.900	62.5	5.63	20.0
0.730	0.933	59.8	5.15	20.1
Pressure 30 Mm.				
0.574	0.873	72.1	5.10	30.0
0.623	0.900	70.9	5.45	30.1
0.731	0.935	68.1	5.29	30.0
Pressure 40 Mm.				
0.471	0.819	81.4	5.08	40.0
0.581	0.870	78.6	4.82	40.1
0.615	0.891	77.0	5.12	40.0
0.622	0.893	77.0	5.07	40.0
Pressure, 50 Mm.				
0.105	0.354	102.9	4.67	50.0
0.105	0.349	102.9	4.57	50.0
0.113	0.309	102.7	3.51	49.7
0.177	0.487	99.3	4.42	50.0
0.186	0.485	99.4	4.12	50.1
0.217	0.549	97.5	4.39	50.1
0.222	0.544	99.3	4.18	50.0
0.255	0.586	95.4	4.14	49.7
0.344	0.710	91.6	4.67	50.0
0.364	0.735	90.4	4.84	50.0
0.365	0.727	90.7	4.63	50.0
0.367	0.711	90.5	4.24	49.7
0.376	0.737	90.1	4.65	50.0
0.376	0.743	...	4.80	50.1
0.379	0.756	90.0	5.08	50.0
0.387	0.719	89.5	4.06	50.0
0.457	0.796	87.2	4.63	49.7
0.459	0.790	87.0	4.43	49.7
0.459	0.800	87.1	4.71	49.7
0.461	0.794	87.1	4.51	49.8
0.463	0.800	87.6	4.64	50.0
0.473	0.814	86.5	4.87	50.0
0.474	0.820	86.5	5.06	50.0
0.474	0.820	87.1	5.06	49.9
0.475	0.808	86.7	4.65	49.9
Pressure, 50 Mm.				
0.479	0.812	86.5	4.70	50.0
0.479	0.835	87.0	5.50	50.0
0.489	0.822	86.1	4.82	49.9
0.491	0.806	85.8	4.30	49.9
0.498	0.819	85.6	4.56	49.9
0.502	0.823	85.5	4.61	49.8
0.531	0.843	84.6	4.74	49.9
0.543	0.863	84.5	5.30	50.0
0.547	0.852	84.2	4.77	50.0
0.548	0.892	83.7	6.81	49.9
0.548	0.864	83.9	5.24	49.9
0.548	0.854	84.7	4.83	50.0
0.595	0.882	82.6	5.09	50.0
0.619	0.889	82.4	5.08	50.0
0.662	0.906	81.1	4.92	50.1
0.730	0.930	79.4	4.91	50.1
0.730	0.926	79.4	4.63	49.9
0.736	0.930	79.2	4.76	50.0
0.782	0.942	78.3	4.53	50.1

x	y	Temp., ° C.	α	Corrected Pressure Mm. Hg
Methyl Caprylate–Methyl Caprate				
Pressure, 30 Mm.				
0.263	0.584	117.2	3.93	30.0
0.430	0.743	111.7	3.83	29.9
0.512	0.813	109.8	4.14	30.2
0.590	0.857	107.2	4.17	30.0
0.706	0.908	104.5	4.11	30.1
0.913	0.975	99.9	3.72	30.0
Pressure, 40 Mm.				
0.265	0.570	124.7	3.68	40.1
0.432	0.750	118.8	3.94	40.0
0.501	0.792	116.9	3.79	40.2
0.590	0.847	113.9	3.85	40.0
0.700	0.903	111.1	3.99	40.0
0.906	0.984	106.5	6.38	40.0
Pressure, 50 Mm.				
0.261	0.523	130.2	3.11	50.1
0.269	0.528	130.1	3.04	50.0
0.424	0.726	124.5	3.60	50.1
0.491	0.788	122.3	3.86	50.1
0.582	0.843	119.4	3.86	50.0
0.705	0.913	116.6	4.39	50.0
0.913	0.966	111.9	2.79	50.0
Pressure, 100 Mm.				
0.276	0.528	148.8	2.91	100.0
0.491	0.767	140.9	3.41	100.1
0.600	0.808	137.7	3.56	100.0
0.605	0.845	137.7	3.71	100.0
0.713	0.899	134.6	3.58	99.9
0.915	0.968	129.5	2.81	99.9
Methyl Caprate–Methyl Laurate				
Pressure, 30 Mm.				
0.289	0.562	147.6	3.16	29.9
0.576	0.830	139.7	3.59	29.9
0.653	0.831	170.8	2.61	30.0
0.872	0.966	133.0	4.17	30.0
Pressure, 40 Mm.				
0.379	0.655	152.4	3.11	40.1
0.580	0.823	139.5	3.37	40.0
0.640	0.857	145.2	3.37	40.0
0.646	0.852	137.9	3.15	40.0
0.828	0.947	141.1	3.69	40.1
Pressure, 50 Mm.				
0.310	0.567	160.3	2.91	50.0
0.551	0.783	153.2	2.94	50.0
0.599	0.823	151.8	3.11	50.0
0.647	0.839	145.0	2.84	50.1
0.822	0.930	146.9	2.98	50.1
Pressure, 100 Mm.				
0.289	0.534	180.6	2.82	100.1
0.449	0.682	175.5	2.63	100.2
0.663	0.860	150.6	3.12	100.1
0.849	0.940	165.6	2.78	100.1
Methyl Laurate–Methyl Myristate				
Pressure, 30 Mm.				
0.190	0.534	179.6	4.88	30.0
0.360	0.602	174.2	2.69	30.2
0.657	0.844	166.7	2.82	30.0
0.844	0.939	162.6	2.84	30.0
0.874	0.950	161.9	2.74	30.0

Table VI. Continued

x	y	Temp., ° C.	α	Corrected Pressure, Mm. Hg
Methyl Laurate–Methyl Myristate (Continued)				
Pressure, 40 Mm.				
0.189	0.411	187.3	3.00	40.0
0.364	0.598	181.7	2.60	40.1
0.651	0.825	174.0	2.52	39.8
0.840	0.939	170.2	2.93	40.0
0.878	0.947	169.2	2.48	39.8
Pressure, 50 Mm.				
0.196	0.424	193.2	3.02	49.8
0.368	0.596	187.8	2.53	50.0
0.646	0.813	180.1	2.38	49.8
0.851	0.934	176.0	2.48	50.1
0.937	0.942	175.2	1.09	50.0
Pressure, 100 Mm.				
0.196	0.503	213.8	4.15	100.0
0.370	0.590	208.3	2.45	100.1
0.651	0.823	200.5	2.49	99.8
0.854	0.935	196.0	2.46	99.8
0.889	0.952	195.3	2.48	99.9
Methyl Myristate–Methyl Palmitate				
Pressure, 30 Mm.				
0.346	0.571	200.6	2.52	29.9
0.492	0.705	196.8	2.47	30.1
0.496	0.734	196.7	2.80	30.0
0.767	0.894	190.8	2.56	29.9
Pressure, 40 Mm.				
0.344	0.585	208.3	2.69	40.1
0.486	0.729	204.6	2.86	40.0
0.492	0.710	204.4	2.53	39.9
0.740	0.873	198.9	2.42	39.9
Pressure, 50 Mm.				
...	0.543	215.0	...	49.9
0.488	0.710	211.0	2.57	49.8
0.492	0.696	210.9	2.36	50.1
0.731	0.834	205.3	1.85	50.0
Pressure, 100Mm.				
0.359	0.565	235.8	2.32	99.8
0.488	0.709	232.4	2.65	99.8
0.496	0.728	232.1	2.72	100.0
0.750	0.876	226.1	2.35	99.7
Methyl Palmitate–Methyl Stearate				
Pressure, 30 Mm.				
0.338	0.583	224.7	2.74	30.0
0.376	0.572	223.9	2.17	29.9
1-Hexanol–1-Octanol				
Pressure, 30 Mm.				
0.396	0.752	92.6	4.62	30.3
0.549	0.838	88.4	4.25	29.9
0.709	0.938	84.7	6.21	30.0
0.824	0.967	82.4	6.26	29.9
Pressure, 50 Mm.				
0.531	0.840	98.5	4.63	50.0
0.400	0.735	102.5	4.16	49.9
0.713	0.916	94.7	4.39	50.1
0.825	0.963	92.4	5.52	50.0
Pressure, 100 Mm.				
0.417	0.722	117.8	3.63	100.0
0.549	0.830	113.4	4.01	99.7
0.707	0.908	109.4	4.19	100.0
0.830	0.949	106.5	3.81	99.8

COMPARISON OF RELATIVE VOLATILITIES PREDICTED BY TWO METHODS

Relative volatilities for the methyl palmitate–methyl stearate system at 30 mm. of Hg total pressure were predicted by two methods. First these values were obtained by extrapolation of the curves relating the relative volatilities of the binary mixtures to the number of carbon atoms as shown in Figure 7 and discussed above. The second method involved the use of experimental vapor pressure data for methyl palmitate and vapor pressure data for methyl stearate predicted by the method of Myers and Fenske. Equilibrium composition and relative volatilities were predicted according to Raoult's and Dalton's laws using the above-mentioned vapor pressure data. Results from the two methods of predicting relative volatilities given below are similar.

	First Method		Second Method,
x	logα	α	α
0.1	0.356	2.27	2.25
0.5	0.361	2.30	2.32
0.9	0.376	2.38	2.39

These results indicate that further predictions could be made with reasonable confidence for other binary mixtures of this homologous series. Additional extrapolation of Figure 7 for the methyl stearate–methyl arachidate system would probably not give the degree of accuracy as the above results because of the curvature in the plot. However, if one vapor pressure–temperature point for methyl arachidate were available, reliable equilibrium data could be obtained by the second method.

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