Vapor-Liquid Equilibria of the Caproic Acid-Caprylic Acid System at 20, 50, and 100 MM. of Mercury Pressure

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Experimental values of vapor-liquid composition equilibrium for mixtures of caproic and caprylic acid at 20, 50, and 100 mm. of mercury pressure are given in Table I. These data were plotted and smooth curves were drawn. The "visually smoothed" data are reported in Table II, along with the activity coefficients calculated from them. Table III gives the values of vapor molecular weight calculated from vapor density measurements. In Table IV the experimental values of vapor-phase mole fraction at 50 mm. of mercury are compared with values calculated from Raoult's law and from the Margules equation. The evidence indicates that caproic acid–caprylic acid mixtures are ideal.

APPARATUS AND PROCEDURE

The apparatus used to obtain the data of Table I was similar to that described by Rose, Papahronis, and Williams (*5*). Several modifications were used, all varieties of the Williams self-lagging still (*6*). For the final measurements the apparatus was fitted with a relatively wide and long Cottrell tube (12 mm. in outside diameter by 450 mm.) packed with 0.24 × 0.24 inch protruded packing. The first series of measurements was made in similar apparatus without packing in the Cottrell tube and also without an agitator in the boiler. The second series of measurements was made with an irregular wire spiral in the Cottrell tube and agitation in the boiler.

Table I. Caproic Acid–Caprylic Acid Binary System. Experimental Vapor-Liquid Equilibrium Values

20 Mm. Hg			50 Mm. Hg			100 Mm. Hg		
x_1	y_1	t, °C.	x_1	y_1	t, °C.	x_1	y_1	t, °C.
0.652	0.881	117.7	0.372	0.681	143.5	0.338	0.638	162.1
0.584	0.861	118.1	0.610	0.841	137.6	0.584	0.826	154.6
0.530	0.834	120.3	0.610	0.848	137.6	0.437	0.719	156.7
0.469	0.796	121.5	0.371	0.652	144.4	0.377	0.677	160.7
0.399	0.738	123.4	0.240	0.521	148.2	0.345	0.627	162.1
0.376	0.719	124.1	0.225	0.499	149.5	0.316	0.610	162.8
0.315	0.654	125.8	0.138	0.367	152.3	0.269	0.558	164.5
0.249	0.586	128.2	0.620	0.850	137.5	0.227	0.487	166.0
0.220	0.533	129.6	0.763	0.916	134.4	0.201	0.473	167.0
0.173	0.462	130.9	0.816	0.940	133.0	0.158	0.397	168.4
0.132	0.386	132.2	0.711	0.893	136.6	0.133	0.329	169.7
0.741	0.925	115.8	0.740	0.909	135.9	0.574	0.811	155.0
			0.673	0.880	137.0	0.643	0.856	153.2
			0.593	0.841	138.8	0.740	0.902	151.0
			0.531	0.804	139.8	0.795	0.931	149.9
			0.484	0.766	141.0			
			0.423	0.714	142.9			

Cottrell tube diameter = 12 mm. o.d.
Cottrell tube length = 450 mm.
Packed with 0.24 × 0.24 inch protruded packing.

EVALUATION OF VAPOR-LIQUID EQUILIBRIUM DATA

The final set of experimental equilibrium measurements is very nearly identical with values calculated by Raoult's law (see Table IV). Negligible heats of mixing and negligible volume change on mixing also confirm the ideality of the system.

The first attempt at measuring $x - y - t$ data gave results which were widely different from those reported here. However, the $x - y$ and $t - x$ plots were smooth and reproducible and the apparatus operated so well that no suspicion would have been aroused if a thermodynamic analysis of the data had not been made. The ensuing apparatus changes and the results obtained permit conclusions about the necessity for thermodynamic analysis and the possibility of accurately predicting $x - y$ values that are difficult to measure experimentally.

One could expect this binary system to follow Raoult's law, because the two molecules are so similar. The first set of experimental measurements is given in Figures 1 and 2. These data, which were obtained at 50 mm. of mercury in a simplified Williams still which had no agitator in the boiler and no packing in the Cottrell tube, not only failed to show ideality but also gave evidence of gross thermodynamic inconsistency.

A calculation of activity coefficients gave the curves shown in Figure 3, which are obviously in disagreement with the Gibbs-Duhem equation. The runs were repeated from time to time in the same equipment and the data were so consistently reproduced that it was deemed worth while to investigate the possibility of association. The activity coefficients had been calculated on the basis of formula weights, which would not be true molecular weights if association occurred.

In the meantime parallel investigation (*5*) gave erratic data on a fatty alcohol binary system with a similar still. Incorporation of an internal heater and a stirrer to promote smoother boiling gave reproducible results in this case. Furthermore, this modification, instituted solely to achieve reproducibility, gave an $x - y$ curve that indicated a greater relative volatility than had been indicated by visual

Table II. Caproic Acid–Caprylic Acid Binary System. Visually Smoothed Experimental Vapor-Liquid Equilibrium Values

	20 Mm. Hg				50 Mm. Hg				100 Mm. Hg			
x_1	y_1	t °C.	γ_1	γ_2	y_1	t °C.	γ_1	γ_2	y_1	t °C.	γ_1	γ_2
0.00	0.000	139.6	. . .	1.000	0.000	158.9	. . .	1.000	0.000	175.4	. . .	1.000
0.10	0.316	134.9	1.006	0.9724	0.280	154.4	0.9856	0.9799	0.256	171.0	0.9738	0.9884
0.20	0.514	130.5	1.000	0.9854	0.466	150.0	0.9768	1.003	0.445	166.9	0.9793	0.9827
0.30	0.644	126.4	1.013	1.036	0.600	146.1	0.9833	1.035	0.590	163.3	0.9871	0.9666
0.40	0.741	123.3	1.015	1.051	0.700	142.8	0.9880	1.066	0.697	160.0	0.9892	0.9620
0.50	0.816	120.7	1.016	1.043	0.779	139.9	0.9959	1.090	0.773	156.9	0.9877	0.9927
0.60	0.870	118.7	0.9986	1.039	0.843	137.6	0.9927	1.090	0.835	154.2	0.9874	1.020
0.70	0.916	116.7	0.9977	1.011	0.892	135.6	0.9838	1.109	0.888	151.8	0.9889	1.031
0.80	0.951	114.8	0.9997	0.9949	0.935	133.8	0.9783	1.102	0.933	149.8	0.9858	1.016
0.90	0.979	113.1	1.000	0.9487	0.969	131.9	0.9825	1.164	0.968	147.8	0.9862	1.068
1.00	1.000	111.5	1.000	. . .	1.000	129.9	1.000	. . .	1.000	145.7	1.000	. . .

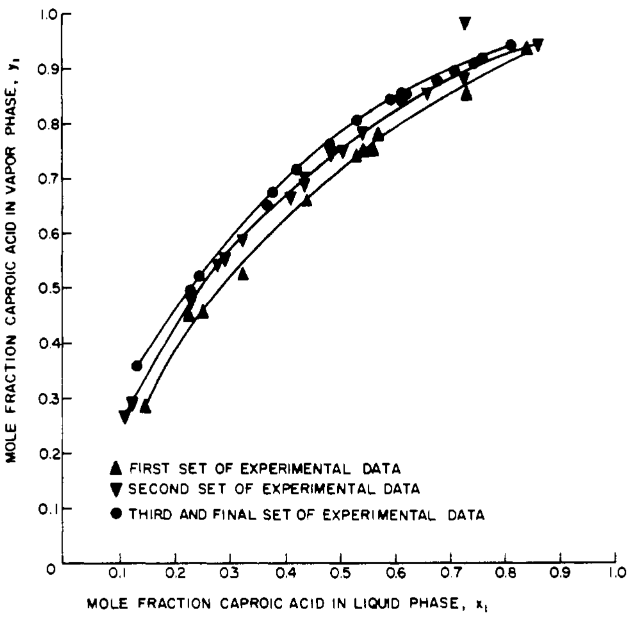

Figure 1. Experimental vapor-liquid equilibrium diagrams for the caproic acid-caprylic acid binary system at 50 mm. of mercury

smoothing of the erratic fatty alcohol data. The following conclusions were drawn.

In a Cottrell-tube apparatus a steady state may be reached in which the vapor and liquid are not in equilibrium. Reproducible nonequilibrium boiling will produce a steady state in the system, because the liquid and vapor, which are separated at the top of the tube, are remixed in the same proportion before they re-enter the still pot. Therefore mere reproducibility is not an evidence of thermodynamic consistency.

Two things must be done to promote attainment of an equilibrium state: boil small bubbles from a well-mixed still pot so that they will be (as nearly as possible) in equilibrium with the liquid; and increase the mixing in the Cottrell tube to promote attainment of composition equilibrium in the event that the boiling did not produce an equilibrium vapor.

The caproic-caprylic acid binary mixture was rerun in an apparatus having a stirrer and internal heater in the still pot and an irregular wire spiral in the Cottrell tube. With this modified apparatus, a second complete set of data was obtained (see Figures 1 and 2).

Figure 3 shows that the second set of experimental data is not in accord with the predictions of the Gibbs-Duhem equation (*2*). The trial-and-error prediction method of Rose and others (*7*) was used to obtain a quantitative measure of the difference between the experimental and predicted equilibrium data. This was 3.8 mole % for vapor compositions. (A similar calculation on the first set of data showed a deviation of 8.1 mole %.) This discrepancy could have occurred for any of the following reasons.

Caproic acid and caprylic acid may associate in the liquid phase.

Caproic acid and caprylic acid may not follow the perfect gas law in the vapor phase.

Caproic acid and caprylic acid may associate in the vapor phase.

The thermodynamic equation chosen for the trial-and-error prediction method may not be applicable to the binary system.

The experimental equilibrium data may still be in error.

LIQUID PHASE ASSOCIATION

An investigation of the possibility of association had already been started before the experience with the fatty alcohol system initiated equipment modifications. It was concluded that the pure components existed in the mono-

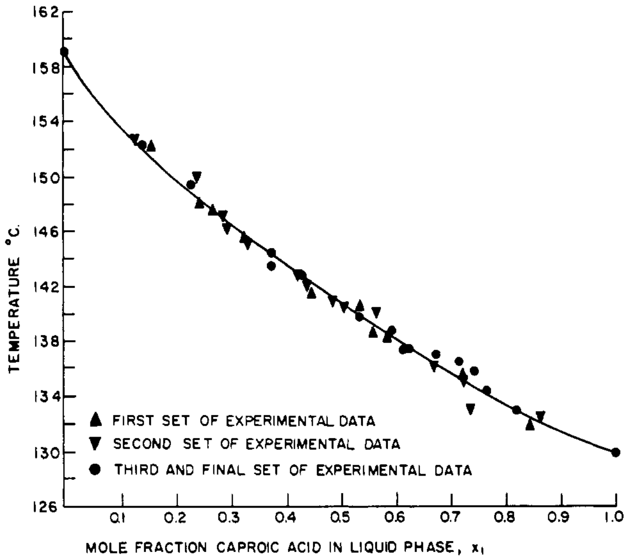

Figure 2. Experimental temperature—composition diagrams for the caproic acid-caprylic acid binary system at 50 mm. of mercury

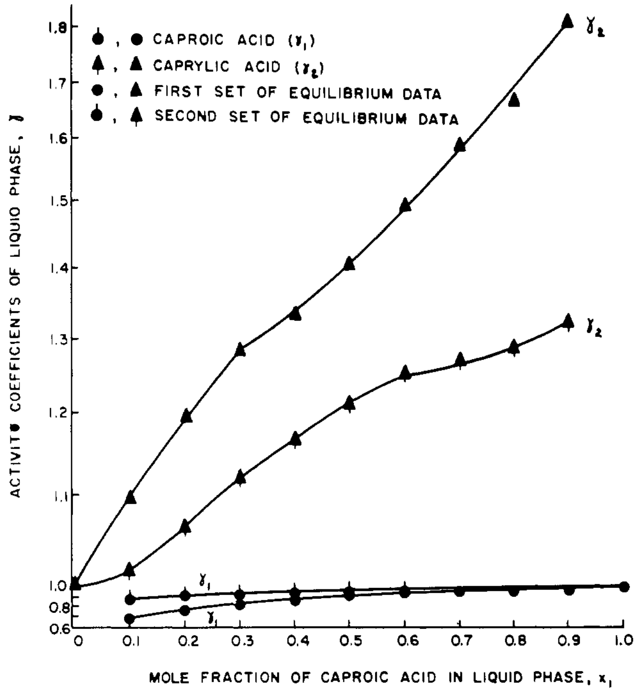

Figure 3. Activity coefficient-composition diagrams for the caproic acid-caprylic acid binary system at 50 mm. of mercury

meric form in the liquid phase between 129.9° to 158.9°C. because the experimental boiling temperatures of the mixtures were equal to the temperatures calculated from Raoult's law.

PERFECT GAS LAW

Critical temperatures and pressures for the pure components were estimated by the method of Hougen and Watson (*3*). These critical constants used in conjunction with the compressibility charts given by Weber (*8*) show the vapors to be ideal. There was little likelihood of gas law deviation at the low pressures involved.

VAPOR PHASE ASSOCIATION

A modified Dumas bulb method was used to determine the molecular weights of the vapors near their boiling points

Table III. Vapor Phase Molecular Weight Determinations for Caproic Acid and Caprylic Acid

π, Mm. Hg	t, °C.	$M_{calcd.}$	Formula Weight
Caproic Acid			
50.0	134.5	117.1	116.1
50.0	135.0	116.5	116.1
50.0	134.7	122.0	116.1
Caprylic Acid			
50.0	165.7	143.2	144.2
50.0	166.9	148.5	144.2
50.0	165.9	144.3	144.2

Table IV. Experimental and Calculated Values of Vapor-Phase Mole Fractions of Caproic Acid-Caprylic Acid Binary System at 50 Mm. of Mercury

Visually Smoothed Experimental Values			Calcd. by Raoult's Law Using Experimental Temperatures		Calcd. from[a] Margules Equation (7)	
x_1	t, °C.	y_1	$\pi_{calcd.}$	$y_{1calcd.}$	$\pi_{calcd.}$	$y_{1calcd.}$
0.10	154.4	0.280	50.94	0.278	51.02	0.281
0.20	150.0	0.466	50.47	0.472	50.91	0.476
0.30	146.1	0.600	49.82	0.612	50.46	0.617
0.40	142.8	0.700	49.49	0.715	50.22	0.719
0.50	139.9	0.779	49.24	0.794	50.00	0.795
0.60	137.6	0.843	49.66	0.854	50.19	0.854
0.70	135.6	0.892	50.20	0.903	50.50	0.900
0.80	133.8	0.935	50.73	0.941	50.83	0.939
0.90	131.9	0.969	50.64	0.973	50.53	0.971
			Δy_{RMS}[b]	0.010		0.011
			$\Delta \pi_{RMS}$	0.60		0.60

[a] Calculated Margules constants $\begin{cases} A = 0.0000 \\ B = 0.0398 \end{cases}$

[b] Root-mean-square deviation between calculated and experimental values.

at 50 mm. of mercury (*1*). The final results indicated the vapors of the pure components to be monomeric (Table III).

APPLICABILITY OF THERMODYNAMIC EQUATION

The Margules equation was selected for the trial-and-error prediction method (*6*) on the basis of the criteria developed by Carlson and Colburn (*2*) after an examination of a large number of systems. They founa that the Margules equation applied to binary mixtures when the molar volumes of the components were nearly equal. The ratio of the molar volumes of caprylic and caproic acids is 1.38 at 80°C.

VALIDITY OF SECOND SET OF EQUILIBRIUM DATA AT 50 MM. OF MERCURY

The results given above required the conclusion that the second set of equilibrium composition data at 50 mm. of mercury was incorrect. As a consequence, the equilibrium apparatus was again modified by filling the Cottrell tube with 0.24 × 0.24 inch protruded packing. A third set of results was obtained with this apparatus, and it was this set that indicated an ideal mixture and exhibited no discrepancies from thermodynamic consistency requirements. In fact, as shown in Table IV, the system was ideal.

The binary mixture was then run at 20 and 100 mm. of mercury. In each case the data showed good agreement with Raoult's law ($\Delta y_{RMS} = 0.004$ at 20 mm. of mercury and 0.0035 at 100 mm. of mercury) and with the Margules equation ($\Delta y_{RMS} = 0.007$ at 20 mm. of mercury and 0.005 at 100 mm. of mercury).

BOILING POINT CURVE

Figure 2 shows the experimental $t - x$ curves for 50 mm. of mercury for the three sets of data. Each apparatus gave the same curve. Table IV compares the y values, predicted from this curve and vapor pressure data by the method of Rose and others (*7*), with the final experimental values. It is obvious that the correct $t - x$ curve is easier to obtain than the correct $x - y$ curve. This is true in this apparatus because the quantity of liquid is very large compared to the quantity of vapor. Vapor composition can probably vary a few mole per cent without appreciably affecting liquid composition.

PURIFICATION OF CAPROIC AND CAPRYLIC ACIDS

The starting materials were commercial grade of about 85 to 95% purity. They were fractionated at high reflux ratio in a 30-plate packed column at pressures of about 50 mm. of mercury. The heart cuts only were used. The high purity of the starting materials was confirmed by determination of acid numbers, iodine numbers (*4*), carbon-hydrogen analyses, Karl Fischer analysis for water, and partial crystallization followed by comparison of the properties of the fractions (*1*).

REFRACTIVE INDEX DETERMINATION

Refractive index was read with a five-place Valentine refractometer with temperature maintained at 25°C. by circulation of water from a thermostatically controlled bath. Corrections were made by comparison with readings of the refractive index of secondary standard liquids that in turn had been carefully checked against liquids certified by the National Bureau of Standards. The refractive index of the caproic acid was 1.41459. That of the caprylic acid was 1.42597. Composition of the equilibrium still samples was determined by refractive index.

NOMENCLATURE

A = constant in Margules equations
B = constant in Margules equations
FW = formula weight
M = molecular weight
n_D^{25} = refractive index at 25°C.
P_0 = vapor pressure of pure component, mm. of mercury
t = temperature in °C.
x = mole fraction in liquid phase
y = mole fraction in vapor phase
Δ = difference between experimental and calculated value
γ = activity coefficient of liquid phase
π = total pressure in mm. of mercury

Subscripts

1 = caproic acid
2 = caprylic acid
calcd. = calculated value
RMS = root-mean-square deviation

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Received for review June 17, 1957. Accepted February 25, 1958.