Experimental Measurement of Vapor-Liquid Equilibria for Octanol-Decanol and Decanol-Dodecanol Binaries

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During the first phases of the work reported herein erratic and nonreproducible results were obtained. Modification of the apparatus was necessary to obtain the final results given in Tables I and II. The data, obtained at pressures of 20, 50, 100, and 300 mm. of mercury, were plotted on *x*-*y* and *t*-*x* diagrams and smooth curves were drawn. The "visually smoothed" data are reported in Tables III and IV. Activity coefficients for both components were also calculated and included in Tables III and IV. They indicate that the systems are ideal.

APPARATUS

The final version of the apparatus is shown in Figure 3, while Figure 2 shows an earlier version that was reasonably satisfactory, and Figure 1 shows the original version. All are modifications of the Williams self-lagging apparatus (9). This general type of apparatus was chosen for the fatty alcohol studies because of extensive difficulties in studying fatty acid and ester equilibria in other types of equilibrium stills (7).

The final measurements on the alcohol mixtures were made with the apparatus shown in Figure 3. The boiler in this apparatus differs from that of Figure 1 in the following respects. It has a flat bottom, so that a magnetically driven stirrer (Teflon-covered iron bar) can be used. An internal heater made of fine Nichrome wire (B. & S. gage 29) is included to increase the bubble formation for the same energy input. This combination of stirrer and fine heating wire (the heater as a nucleator and the agitator to shear the bubbles from the heater before agglomeration occurred) provided a froth of small bubbles, as compared with a smaller number of large bubbles in the earlier design. The centrifugal action of the stirrer drew the low density vapor toward the center of the boiler beneath the Cottrell tube, eliminating a random motion of the vapor bubbles experienced in earlier models. This resulted in smoother Cottrell action, and eliminated surges due to sudden increases or decreases in the effective head of fluid in the Cottrell tube. Improved heat transfer and mixing of the recycled fluid with the reboiler contents was effected by the stirrer. It also helped to promote a steady boilup rate and delivery of constant composition fluid into the Cottrell tube.

The use of stopcocks was entirely eliminated in the apparatus of Figure 3. Samples for analysis were obtained from its sample chambers by means of a pipet introduced from above after releasing the vacuum to stop boiling action and removing the closure caps. All chance of mixing of liquids, by backflow into the vapor and liquid sample chambers, was eliminated by introducing overflow traps in the return lines beyond the sample chambers.

The apparatus shown in Figure 3 is self-lagging for moderately high temperatures. However for these systems, which boil between 100° and 250°C., it was deemed

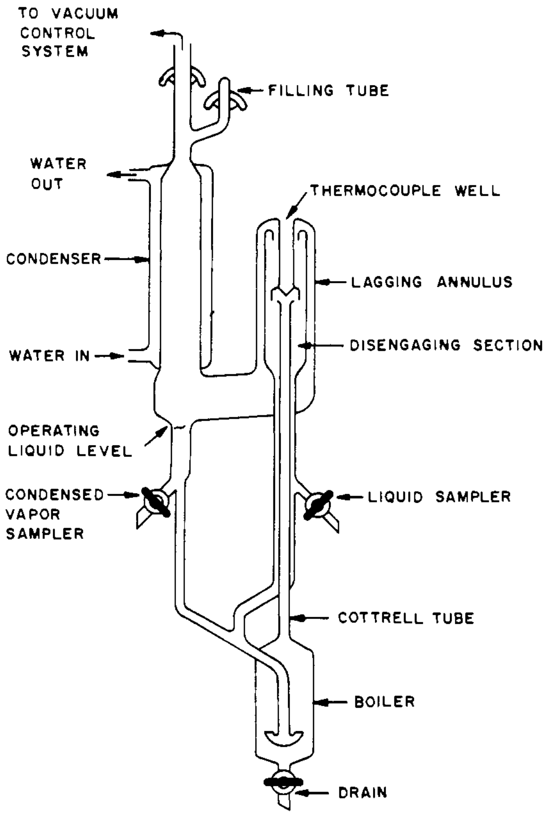

Figure 1. Simplified self-lagging still without stirrer

Table I. Octanol-Decanol Binary
Experimental Vapor-Liquid Equilibrium Values Determined in Apparatus Shown in Figure 2

20 Mm. Hg Pressure			50 Mm. Hg Pressure			100 Mm. Hg Pressure			300 ± 2.0 Mm. Hg Pressure		
x_1	y_1	t, °C.	x_1	y_1	t, °C.	x_1	y_1	t, °C.	x_1	y_1	t, °C.
0.817	0.936	103.8	0.171	0.431	138.7	0.893	0.971	136.6	0.218	0.421	185.9
0.816	0.937	103.8	0.187	0.458	138.7	0.897	0.968	136.7	0.227	0.418	185.7
0.618	0.859	107.9	0.258	0.572	135.6	0.725	0.912	139.7	0.379	0.631	180.2
0.607	0.861	107.8	0.263	0.572	135.6	0.725	0.905	139.8	0.405	0.657	180.1
...	...	...	0.417	0.716	131.1	0.573	0.827	144.0	0.404	0.657	179.2
...	...	...	0.459	0.762	130.1	0.574	0.827	144.0	0.570	0.783	174.0
0.345	0.657	114.4	0.595	0.849	126.6	0.352	0.649	149.5	0.570	0.774	174.1
0.349	0.664	114.3	0.883	0.965	120.7	0.240	0.499	153.5	0.719	0.862	170.0
0.227	0.532	117.8	...	...	...	0.218	0.470	154.0	0.714	0.850	170.6
0.226	0.522	117.6	...	...	...	...	...	...	0.799	0.885	168.1
0.130	0.352	121.0	...	...	...	...	...	...	0.808	0.912	168.3

Table II. Decanol-Dodecanol Binary
Experimental Vapor-Liquid Equilibrium Values Determined in Apparatus Shown in Figure 3

20 Mm. Hg Pressure			50 Mm. Hg Pressure			100 Mm. Hg Pressure			300 ± 2.5 Mm. Hg Pressure[a]		
x_1	y_1	t, °C.	x_1	y_1	t, °C.	x_1	y_1	t, °C.	x_1	y_1	t, °C.
0.096	0.230	149.7	0.042	0.083	173.3	0.157	0.307	186.7	0.898	0.945	200.0
0.081	0.215	149.6	0.081	0.193	171.4	0.200	0.369	185.9	0.882	0.946	199.8
0.167	0.384	146.1	0.100	0.257	170.2	0.327	0.544	180.8	0.712	0.874	202.7
0.171	0.394	146.3	0.145	0.323	168.9	0.365	0.574	180.3	0.709	0.865	202.5
0.288	0.555	142.4	0.193	0.416	166.5	0.357	0.593	179.8	0.539	0.713	206.6
0.304	0.571	142.4	0.230	0.453	165.8	0.414	0.660	177.8	0.539	0.754	207.6
0.442	0.713	138.6	0.314	0.578	163.0	0.483	0.730	176.4	0.449	0.659	211.0
0.431	0.713	138.5	0.351	0.609	161.7	0.485	0.714	176.5	0.449	0.661	211.6
0.557	0.799	135.6	0.451	0.713	158.9	0.534	0.753	174.6	0.353	0.550	215.0
0.564	0.797	135.6	0.498	0.743	157.7	0.572	0.800	173.8	0.307	0.491	216.0
0.640	0.837	133.6	0.568	0.800	155.8	0.591	0.799	173.8	...	...	...
0.640	0.844	133.6	0.611	0.820	155.0	0.625	0.812	172.7	...	...	...
0.732	0.885	131.5	0.695	0.879	153.2	0.677	0.866	171.5	...	...	...
0.746	0.896	131.7	0.780	0.914	151.6	0.713	0.878	170.8	...	...	...
0.880	0.958	129.5	0.847	0.943	150.4	0.834	0.942	168.0	...	...	...
0.882	0.955	129.6	0.869	0.945	149.5	0.906	0.960	166.3	...	...	...
...	...	...	0.945	0.976	148.5	...	...	...	...	...	...

[a] Apparatus in Figure 2 used.

Table III. Octanol-Decanol Binary
Visually Smoothed Experimental Vapor-Liquid Equilibrium Values

	20 Mm. Hg				50 Mm. Hg			
x_1	y_1	t, °C.	γ_1	γ_2	y_1	t, °C.	γ_1	γ_2
0.20	0.490	118.7	1.005	1.012	0.472	138.1	1.039	1.020
0.30	0.641	115.4	1.027	0.974	0.618	134.7	1.045	0.985
0.40	0.733	112.4	1.016	1.005	0.717	131.5	1.039	0.988
0.50	0.805	110.0	1.011	1.021	0.792	128.8	1.034	1.000
0.60	0.860	107.8	1.006	1.052	0.851	126.5	1.023	0.997
0.70	0.905	105.9	0.998	1.072	0.898	124.4	1.004	1.010
0.80	0.941	104.0	1.007	1.109	0.935	122.3	1.013	1.072

	100 Mm. Hg				300 Mm. Hg			
0.20	0.430	155.0	0.985	1.060	0.385	186.8	0.945	1.062
0.30	0.585	151.3	1.038	1.030	0.535	182.8	0.969	1.057
0.40	0.698	148.0	1.042	1.000	0.645	179.1	0.999	1.068
0.50	0.778	145.2	1.034	1.028	0.732	176.1	0.994	1.072
0.60	0.839	143.0	1.018	0.998	0.801	173.3	0.995	1.101
0.70	0.888	140.7	1.010	1.025	0.860	170.8	0.991	1.131
0.80	0.928	138.5	1.007	1.042	0.910	168.3	1.000	1.209

Table IV. Decanol-Dodecanol Binary
Visually Smoothed Experimental Vapor-Liquid Equilibrium Values

	20 Mm. Hg				50 Mm. Hg			
x_1	y_1	t, °C.	γ_1	γ_2	y_1	t, °C.	γ_1	γ_2
0.20	0.435	145.0	0.988	1.006	0.413	166.8	0.969	1.016
0.30	0.573	141.8	0.997	1.012	0.556	163.3	0.987	1.004
0.40	0.680	139.1	1.002	1.020	0.661	160.3	0.983	1.020
0.50	0.758	136.7	1.000	1.050	0.745	157.6	0.981	1.029
0.60	0.825	134.6	0.997	1.043	0.814	155.1	0.988	1.047
0.70	0.878	132.7	0.996	1.073	0.872	153.0	1.000	1.059
0.80	0.924	131.0	0.992	1.089	0.922	151.0	1.022	1.081

	100 Mm. Hg				300 Mm. Hg			
0.20	0.378	185.2	0.920	1.048	0.357	219.6	0.893	1.029
0.30	0.530	181.6	0.974	1.039	0.505	216.3	0.939	1.000
0.40	0.645	178.7	0.982	1.026	0.622	213.0	0.967	0.983
0.50	0.731	176.1	0.975	1.030	0.714	210.0	0.967	0.973
0.60	0.802	173.6	0.973	1.045	0.790	207.2	0.964	0.973
0.70	0.861	171.3	0.975	1.070	0.852	204.2	0.972	1.000
0.80	0.915	169.0	0.984	1.075	0.906	201.6	0.978	1.048

advisable to enclose the disengaging section in an insulated heated jacket. The temperature of that jacket was maintained slightly below that of the boiling point of the mixture.

Although the design in Figure 3 provided the most reproducible results, many of the data were measured with the apparatus in Figure 2. This was satisfactory for some mixtures and pressures. It lacked overflow traps and pipet sampling arrangements, but contained an irregularly bent Nichrome wire in the Cottrell tube to provide turbulence and increased contact and thus improved opportunity for reaching composition equilibrium. Reproducibility was limited by occasional contamination of the vapor samples by backflow of the liquid sample during sampling.

With the original apparatus of Figure 1 it was impossible to attain smooth boiling and regular Cottrell action with the fatty alcohol binaries.

EXPERIMENTAL PROCEDURE

The mixture to be studied was charged into the apparatus at a level such that the thermal expansion from room temperature to the boiling point raised the level approximately to the midpoint of the Cottrell tube. This level, according to Cottrell (2), is desirable for "good" Cottrell action.

The heat for boiling was supplied primarily by the internal heater. An external heater wrapped around the boiler was used to prevent heat leak from its walls. The system pressure was maintained by an oil vacuum pump and a regulated nitrogen bleed to a manifold joining the various parts of the apparatus.

After steady Cottrell action was obtained, the heat to the adiabatic jacket (around the disengaging section) was regulated to keep it slightly below the equilibrium temperature. Condensation of vapors in the annulus maintained adiabatic conditions within the disengaging chamber.

Measurements of pressure and temperature were made every 10 minutes. When four consecutive measurements coincided, within the precision of reading, the boiling was stopped by introducing nitrogen to the manifold by a quick opening valve connected to an auxiliary nitrogen reservoir at atmospheric pressure. Samples of the liquid and vapor were then removed for analysis.

The pipet samplers were filled with nitrogen to prevent the moisture in the atmosphere from contacting the samples. With the stopcock samplers a nitrogen blanket was used to prevent water contamination.

A part of the charge was removed through the drain tube and replaced by one of the pure components to cause the desired change in composition for the next determination.

Table V. Decanol-Dodecanol Binary at 50 Mm. of Mercury Comparison of Experimental and Calculated Values of Vapor Phase Mole Fractions and Total Pressure

Visually Smoothed Experimental Values			Calculated			
			Raoult's law, experimental temperatures		van Laar equation (*10*)[a]	
x_1	t, °C.	y_1	$\pi_{\text{calcd.}}$, mm. Hg	$y_{1\text{calcd.}}$	$\pi_{\text{calcd.}}$	$y_{1\text{calcd.}}$
0.10	170.6	0.233	50.29	0.243	50.61	0.249
0.20	166.8	0.413	50.24	0.424	50.80	0.429
0.30	163.3	0.556	49.92	0.561	50.46	0.565
0.40	160.3	0.661	49.64	0.667	50.21	0.670
0.50	157.6	0.745	49.55	0.753	49.99	0.753
0.60	155.1	0.814	49.30	0.822	49.64	0.821
0.70	153.0	0.872	49.33	0.879	49.58	0.877
0.80	151.0	0.922	49.26	0.926	49.41	0.924
0.90	149.1	0.962	49.02	0.966	49.09	0.965
			Δy_{RMS}[b]	= 0.0079	Δy_{RMS}	= 0.0096
			$\Delta\pi_{\text{RMS}}$	= 0.510	$\Delta\pi_{\text{RMS}}$	= 0.554 mm. Hg

[a] Calcd. van Laar constants: $A = 0.00862$, $B = 0.023068$.
[b] RMS denotes root-mean-square deviation between calculated and experimental values.

DISCUSSION

Table V shows the calculated equilibrium vapor composition for the decanol-dodecanol binary at 50 mm. of mercury, assuming ideal behavior of both components in the liquid and vapor—i.e., Raoult's and Dalton's laws were assumed applicable. The calculations were made by using the vapor pressures at the experimental temperature corresponding to a particular liquid mole fraction in the equation $y = \dfrac{P_0x}{\Sigma P_0x}$. The results are in agreement with the experimental values. Similar calculations at the other pressures and for the octanol-decanol binary also indicated compliance with Raoult's law.

Table V also shows the vapor compositions predicted by the method of Rose and others (*10*). These also are in agreement with the experimental values.

The scatter in some of the final results is due largely to the comparatively narrow spread of refractive index between the two components. Precision of analysis was limited because 1 mole % was equivalent to only about 0.00006 and 0.00008 unit of refractive index for the decanol-dodecanol and octanol-decanol mixtures, respectively. A few widely divergent values resulted from measurements made with apparatus not fitted with all the refinements described in a preceding paragraph. It was not considered worth while to repeat these measurements with the improved apparatus, once the general conclusion regarding ideality had been reached from examination of the other results.

VAPOR PRESSURE MEASUREMENTS OF PURE ALCOHOLS

Thermodynamic correlation of isobaric vapor-liquid equilibrium data requires vapor pressure data for the pure compounds over the temperature range involved.

The vapor pressure–temperature relationships of octanol, decanol, and dodecanol were therefore experimentally determined in the self-lagging still.

The still was filled with the pure liquid at room temperature, so that the liquid level was midway between the still pot and the sample stopcocks. The pressure was adjusted to the lowest pressure desired in any particular run and the heat was adjusted until good Cottrell action was achieved. When temperature and pressure were constant within the precision of reading for 15 minutes, it was assumed that thermal equilibrium had been attained and the values were recorded. This was repeated for successively higher pressures until the highest pressure desired was reached. Then

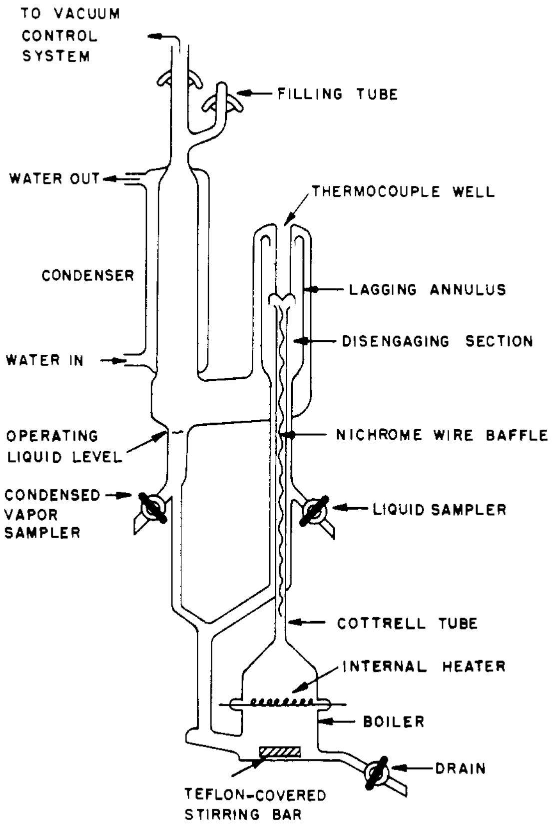

Figure 2. Simplified self-lagging still with stirrer

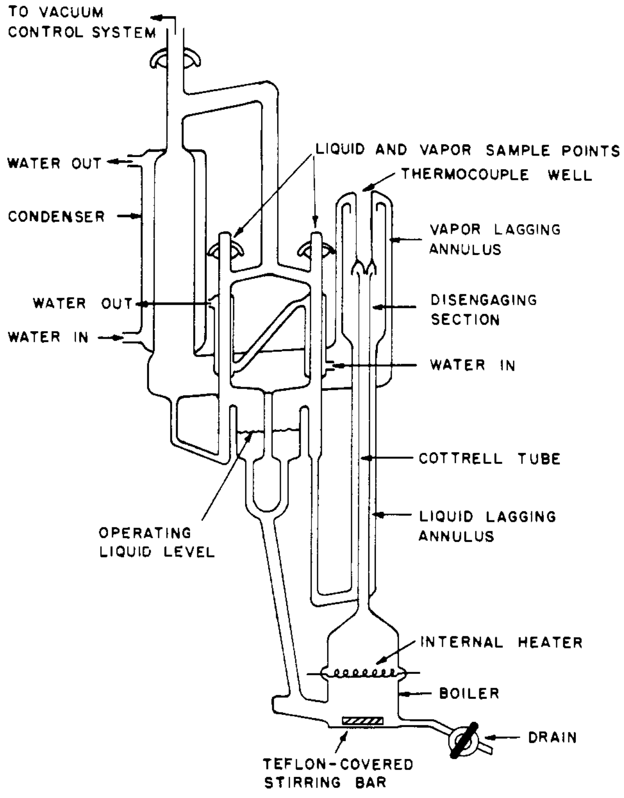

Figure 3. Self-lagging still with stirrer and segregated liquid and vapor sample chambers

the procedure was repeated, but by decreasing the pressure. If contamination or decomposition had occurred, the two sets of data for increasing and decreasing pressures would not coincide. There was no evidence of such ill effects in any of these experiments.

The experimental vapor pressure data are given in Table VI along with Antoine equation constants calculated by the method of Rose and others (*6*). The Antoine equation has the form:

$$\log_{10} P = A - \frac{B}{t + C}$$

The data are in close agreement with those obtained by Krafft (*3, 4*) by determination of boiling points at 15 mm. of mercury. No other experimental measurements of vapor pressures for these alcohols are recorded in the literature, although Stage and Stull (*11, 12*) give values which were determined by correlating the measurements of Krafft by means of a Cox chart. These correlated values are in fair agreement with the measured values of the present paper.

Table VI. Experimental Values of Vapor Pressure

Octanol		Decanol		Dodecanol	
P_0, mm. Hg	t, °C.	P_0, mm. Hg	t, °C.	P_0, mm. Hg	t, °C.
12.20	91.9	2.2	90.9	9.9	138.1
13.50	93.9	5.4	104.4	13.5	143.6
14.30	94.9	9.0	112.6	15.2	147.1
23.90	104.6	10.1	114.7	16.85	149.5
25.70	105.8	17.2	124.9	19.7	152.8
32.70	110.4	25.6	133.0	28.8	161.5
38.65	113.8	33.6	139.0	30.9	163.1
52.00	120.1	36.4	140.6	35.3	166.1
60.80	123.4	39.0	142.1	37.5	167.7
70.30	126.8	44.6	145.2	45.5	173.1
80.90	130.1	44.9	145.2	56.1	177.8
96.50	134.2	45.1	145.6	71.2	184.0
117.30	139.0	45.4	145.6	77.8	186.4
134.3	142.3	52.5	149.0	84.4	188.7
146.0	144.5	62.6	153.7	96.9	192.5
153.2	145.7	70.8	156.9	111.6	196.8
170.0	148.5	97.3	164.3	122.7	199.6
182.1	150.3	113.8	168.4	138.3	202.5
192.8	151.8	133.3	172.9	161.6	207.7
211.0	154.3	154.7	176.9	199.9	214.2
		175.7	180.7		
A^{a} = 7.041743		205.2	184.9	A = 7.53986	
B = 1411.677		225.6	188.4	B = 2003.289	
C = 144.944				C = 168.128	
		A = 7.13936			
		B = 1595.993			
		C = 145.442			

[a] *A, B,* and *C* are Antoine equation constants, calculated by method of Rose and others (*6*).

PURIFICATION AND PURITY OF MATERIALS

Commercial stocks of decanol and dodecanol were purified by precision vacuum distillation. The column used was 2 inches in diameter and was packed to a 35-inch height with 0.16 × 0.16 inch protruded packing. It was operated at 20 to 40 mm. of mercury head pressure and at a reflux ratio of about 40 to 1. Agitation in the still, either by a vertical umbrella-type agitator (*8*) or by a nitrogen bleed, was satisfactory for periods up to nearly 100 hours.

The refractive index (n_D) of dodecanol taken as product from heart cuts was 1.44098 ± 0.00002 and for decanol it was 1.43529 ± 0.00002 at 25 °C. Bonhorst (*1*) reports values of 1.44078 and 1.43516.

Contamination by water, which lowered the refractive index of the distillate product when present even in very minute amounts, was avoided by use of a dry nitrogen blanket during collection and subsequent handling of the alcohols. Severe bumping occurs in the equilibrium apparatus when water is present.

The *n*-octyl alcohol was obtained in high purity from Applied Science Laboratories, Inc., where the method of purification described above was used. The refractive index of the pure octanol was 1.42727 ± 0.00002 at 25 °C. Bonhorst (*1*) reports a value of 1.42719.

Distillations of each alcohol were made at several different pressures to establish that the product recovered was not an azeotrope. There being no change in refractive index with pressure it was concluded that the product was pure alcohol.

NOMENCLATURE

A = constant in Antoine equation (in Table V only, constant in van Laar equation)
B = constant in Antoine equation (in Table V only, constant in van Laar equation)
C = constant in Antoine equation
P_0 = vapor pressure of pure component, mm. of mercury
t = temperature, °C.
π = total pressure, mm. of mercury
γ = activity coefficient, liquid phase, $= \frac{\pi y}{P_0 x}$
x = liquid composition, mole fraction
y = vapor composition, mole fraction
Δ = a difference

Subscripts

1 = more volatile component
2 = less volatile component
calcd. = root-mean-square value
n_D^{25} = refractive index at 25 °C.
α = relative volatility, $\frac{(x_1)(y_2)}{(y_1)(x_2)}$

LITERATURE CITED

(1) Bonhorst, C. W., Ph.D. thesis, Pennsylvania State University, University Park, Pa., 1949.
(2) Cottrell, F. G., *J. Am. Chem. Soc.* **41**, 724 (1919).
(3) Krafft, *Ber.* **16**, 1714-26 (1883).
(4) *Ibid.*, **19**, 2218-23 (1886).
(5) Lange, N. A., "Handbook of Chemistry," Handbook Publishers, 7th ed., 1949.
(6) Rose, Arthur, Acciarri, J. A., Johnson, R. C., Sanders, W. W., *Ind. Eng. Chem.* **49**, 104-9 (1957).
(7) Rose, Arthur, Acciarri, J. A., Williams, E. T., *Ind. Eng. Chem., Chem. Eng. Data Series* **3**, No.2,210 (1958).
(8) Rose, Arthur, Sanders, W. W., *Anal. Chem.* **27**, 331 (1955).
(9) Rose, Arthur, Williams, E. T., *Ind. Eng. Chem.* **47**, 1528-33 (1955).
(10) Rose, Arthur, Williams, E. T., Sanders, W. W., Heiny, R. L., Ryan, J. L., *Ibid.*, **45**, 1568 (1953).
(11) Stage, H., *Fette u. Seifen* **53**, 677-82 (1951).
(12) Stull, D. R., *Ind. Eng. Chem.* **39**, 517-50 (1947).

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