Styrene-Ethylbenzene Vapor-Liquid Equilibria at Reduced Pressures

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Styrene monomer is commonly manufactured by the catalytic dehydrogenation of ethylbenzene. The crude dehydrogenated material containing about 37% styrene is purified by fractionation at low pressure in order to avoid styrene polymerization difficulties. The knowledge of the behavior of styrene-ethylbenzene mixture at subatmospheric pressures is, therefore, essential for this operation. White (*9*) reported vapor-liquid equilibrium data for the ethylbenzene-styrene system at 100 mm. of mercury absolute. This investigation was initiated to develop data for this system at various other subatmospheric pressures.

MATERIALS

The ethylbenzene and styrene used in this study were obtained from the Monsanto Chemical Co. The purity of both compounds was checked by refractive index, density, and boiling point at various pressures. Results of the tests and comparison with literature values (*1*, *2*, *8*) are given in Table I. No effort was made to increase the purity of materials as they were considered to be sufficiently pure. Styrene monomer contained 12 p.p.m. of *p-tert*-butylcatechol (TBC) as polymerization inhibitor.

Table I. Properties of Materials

	Styrene		Ethylbenzene	
	Exptl.	Lit.	Exptl.	Lit.
n_D^{30}	1.5410	1.5408 (*2*)	1.4905	1.4906 (*2*)
d_4^{25}	0.9014	0.9012 (*2*)	0.8622	0.8626 (*2*)
B.P., °C., at 100 mm. Hg	82.19	82.19 (*1*)	74.10	74.11 (*8*)

Table II. Vapor Pressure

	B.P. °C.				
Mm. Hg.	Exptl.	Lit. (*8*)			Lit. (*3*)
		Ethylbenzene			
10	25.88	25.88			25.88
20	38.58	38.60			38.58
30	46.64	46.69			46.62
40	52.73	52.75			52.69
50	57.67	57.66			57.59
60	61.81	61.80			...
100	74.10	74.11			...
200	92.70	92.68			...
		Styrene			
		Lit. (*1*)	Lit. (*5*)	Lit. (*6*)	Lit. (*8*)
10	32.40	33.42	32.72	30.8	35.70
20	45.60	46.15	45.96	44.6	46.53
30	53.86	54.36	54.33	...	54.695
40	60.05	60.52	60.59	59.8	60.82
50	65.45	65.49	65.64	...	65.76
60	69.68	69.70	69.89	69.5	69.95
80	76.60	76.60	76.86	...	76.81
100	82.19	82.19	82.50	82.0	82.38

SELECTION OF VAPOR PRESSURE DATA

The vapor pressure–temperature data of ethylbenzene and styrene were determined in the Colburn still (*4*) under equilibrium conditions. Both experimental and literature data (*1*, *3*, *5*, *6*, *8*) are tabulated in Table II.

In order to be consistent in calculations involving vapor-liquid equilibrium relations, the vapor pressure equations used should be able to reproduce the experimental data. It

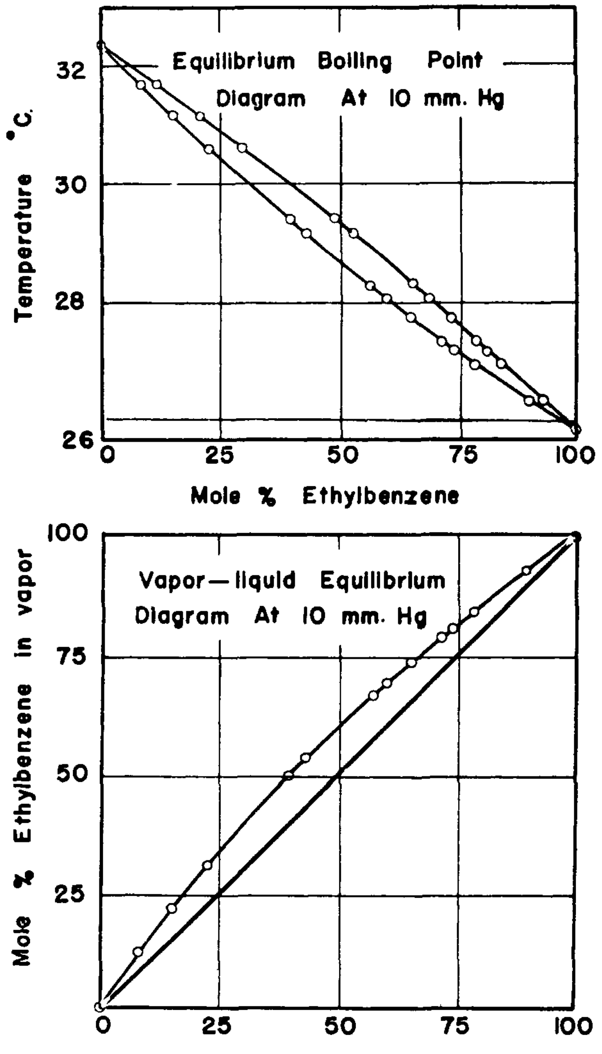

Figure 1. Ethylbenzene-styrene at 10 mm. of mercury

is indicated in Table II that a given vapor pressure equation does not necessarily express the vapor pressure-temperature relation over wide ranges of temperature. The vapor pressures of ethylbenzene calculated at various temperatures above 50 °C. using the Antoine equation (*8*)

$$\text{Log } P \text{ (mm. Hg)} = 6.95719 - \frac{1424.255}{213.206 + t\,°\text{C.}}$$

and at other lower temperatures using the equation (*3*)

$$\text{Log } P \text{ (mm. Hg)} = \frac{2959.08}{T\,°\text{K.}} - 5.8 \log T\,°\text{K.} + 25.25883$$

showed satisfactory agreement with experimental data. The vapor pressure equation for styrene (*1*)

$$\text{Log } P \text{ (mm. Hg)} = 6.95711 - \frac{1445.58}{209.43 + t\,°\text{C.}}$$

was used at various temperatures above 60 °C. At temperatures below 60 °C., none of the vapor pressure equations from the literature gave calculated results which reproduced the experimental data. A vapor pressure equation of the

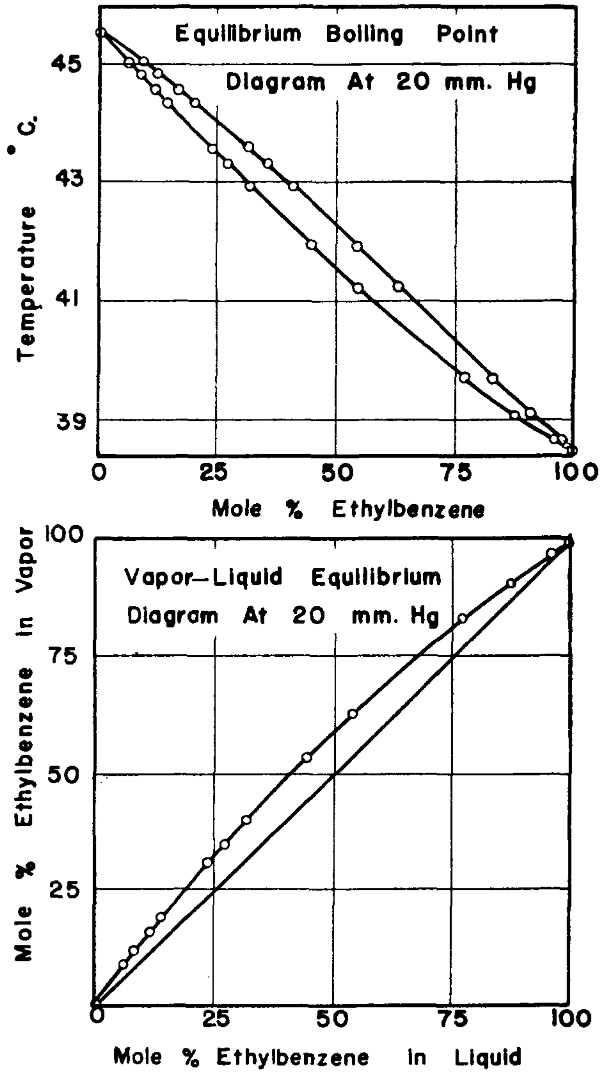

Figure 2. Ethylbenzene-styrene at 20 mm. of mercury

Table III. Vapor-Liquid Equilibrium Data for Ethylbenzene-Styrene System

Temp., °C.	Experimental Data		Smoothed Data		Calculated Data	
	x_1	y_1	x_1	y_1	P_T	y_1
Total Pressure = 10 Mm. Hg Absolute						
25.88	1.000	1.000	1.000	1.000	10.00	1.000
26.24	0.8935	0.925	0.896	0.9263	9.98	0.926
26.92	0.777	0.835	0.785	0.842	9.99	0.8418
27.21	0.7305	0.797	0.739	0.8045	10.00	0.8049
27.30	0.715	0.785	0.725	0.7929	10.01	0.7932
27.73	0.6505	0.732	0.655	0.734	10.00	0.734
28.04	0.6050	0.695	0.605	0.690	10.00	0.690
28.27	0.575	0.6625	0.575	0.662	10.02	0.6627
29.15	0.433	0.535	0.435	0.5288	10.00	0.5280
29.40	0.396	0.5075	0.400	0.4924	10.00	0.4920
30.60	0.222	0.310	0.230	0.305	10.00	0.3020
31.13	0.150	0.220	0.155	0.212	9.98	0.2104
31.68	0.0825	0.128	0.085	0.120	9.98	0.1192
32.40	0.000	0.000	0.000	0.000	10.00	0.0000
20 Mm. Hg						
38.58	1.000	1.000	1.000	1.000	20.00	1.000
38.70	0.965	0.975	0.960	0.972	19.95	0.9719
39.10	0.874	0.910	0.870	0.9065	19.80	0.9061
39.75	0.755	0.825	0.769	0.8275	19.82	0.8274
41.30	0.545	0.630	0.540	0.628	19.84	0.6275
41.98	0.460	0.535	0.441	0.537	19.85	0.5354
42.95	0.335	0.4055	0.318	0.405	19.89	0.4007
43.37	0.2715	0.355	0.270	0.350	19.95	0.3464
43.62	0.2405	0.318	0.235	0.312	19.93	0.3056
44.40	0.139	0.201	0.141	0.1945	19.97	0.1903
44.60	0.115	0.162	0.1200	0.1650	20.00	0.1630
44.90	0.0782	0.120	0.0875	0.120	20.03	0.1203
45.10	0.0555	0.090	0.065	0.0905	20.04	0.0903
45.60	0.000	0.000	0.000	0.000	20.00	0.0000
50 Mm. Hg						
57.67	1.000	1.000	1.000	1.000	50.00	1.000
58.03	0.928	0.945	0.930	0.950	49.78	0.9498
58.40	0.874	0.904	0.875	0.909	49.76	0.9088
59.60	0.726	0.774	0.709	0.776	49.80	0.7759
59.90	0.685	0.746	0.670	0.7426	49.83	0.7425
60.80	0.571	0.644	0.555	0.640	49.91	0.6387
61.30	0.500	0.585	0.495	0.5829	49.99	0.5813
62.20	0.390	0.478	0.386	0.472	50.07	0.4705
62.45	0.360	0.438	0.355	0.439	50.11	0.4378
63.00	0.295	0.365	0.290	0.367	50.15	0.3665
63.95	0.175	0.241	0.181	0.2385	50.15	0.2374
64.76	0.0885	0.1222	0.090	0.123	50.18	0.1222
65.10	0.055	0.075	0.050	0.070	50.14	0.0690
65.60	0.000	0.000	0.000	0.000	50.00	0.0000
100 Mm. Hg						
74.10	1.000	1.000	1.000	1.000	100	1.000
74.37	0.9357	0.9505	0.944	0.960	99.49	0.9589
74.90	0.8498	0.882	0.855	0.890	99.06	0.8908
75.63	0.7405	0.795	0.750	0.806	98.89	0.8055
76.63	0.6100	0.6815	0.619	0.692	98.90	0.6914
77.55	0.5060	0.585	0.506	0.586	99.01	0.5851
78.35	0.418	0.4875	0.410	0.4895	99.08	0.4887
79.12	0.333	0.400	0.323	0.3968	99.25	0.3959
79.30	0.315	0.380	0.3002	0.3720	99.20	0.3707
79.62	0.2703	0.3375	0.269	0.339	99.40	0.3355
80.35	0.185	0.2375	0.188	0.2445	99.50	0.2409
80.85	0.133	0.174	0.135	0.179	99.60	0.1760
81.75	0.042	0.0588	0.045	0.0614	99.93	0.0605
82.19	0.000	0.000	0.000	0.000	100	0.0000
200 Mm. Hg						
92.70	1.000	1.000	1.00	1.00	200.00	1.000
93.4	0.892	0.920	0.88	0.905	198.80	0.9079
94.2	0.7953	0.911	0.78	0.82	199.06	0.8264
94.85	0.693	0.751	0.695	0.750	198.95	0.7535
95.65	0.588	0.650	0.592	0.655	198.78	0.6603
96.42	0.489	0.5585	0.499	0.5675	198.82	0.5714
97.00	0.433	0.501	0.4245	0.493	198.48	0.4966

Antoine form was developed by the author to fit the experimental data at temperatures below 60°C. for styrene as

$$\text{Log } P \text{ (mm. Hg)} = 8.26960 - \frac{2221.3}{T\,^\circ\text{K.}}$$

PROCEDURE

Vapor liquid equilibrium data were obtained through the use of a Colburn equilibrium still (*4*). The still and its operation were described by Rasmussen (*7*).

The still was operated under steady-state conditions of constant liquid levels, constant temperature, and constant pressure. The samples taken for analysis were tested for the presence of styrene polymer after each run. The test consisted of adding an equal amount of anhydrous methanol to the sample solution. The presence of styrene polymer was shown by the turbidity of the mixture after vigorous shaking. When there was any polymer present in the sample, the run was discarded and a new run was made.

The equilibrium samples were analyzed for compositions by means of a Bausch & Lomb precision refractometer using a sodium D-line light source. A calibration curve was constructed by preparing mixtures of definite compositions and obtaining their refractive indices at 30°C. Temperatures were measured by means of a calibrated thermocouple in conjunction with a Leeds & Northrup potentiometer. Pressures were measured by an inclined mercury manometer.

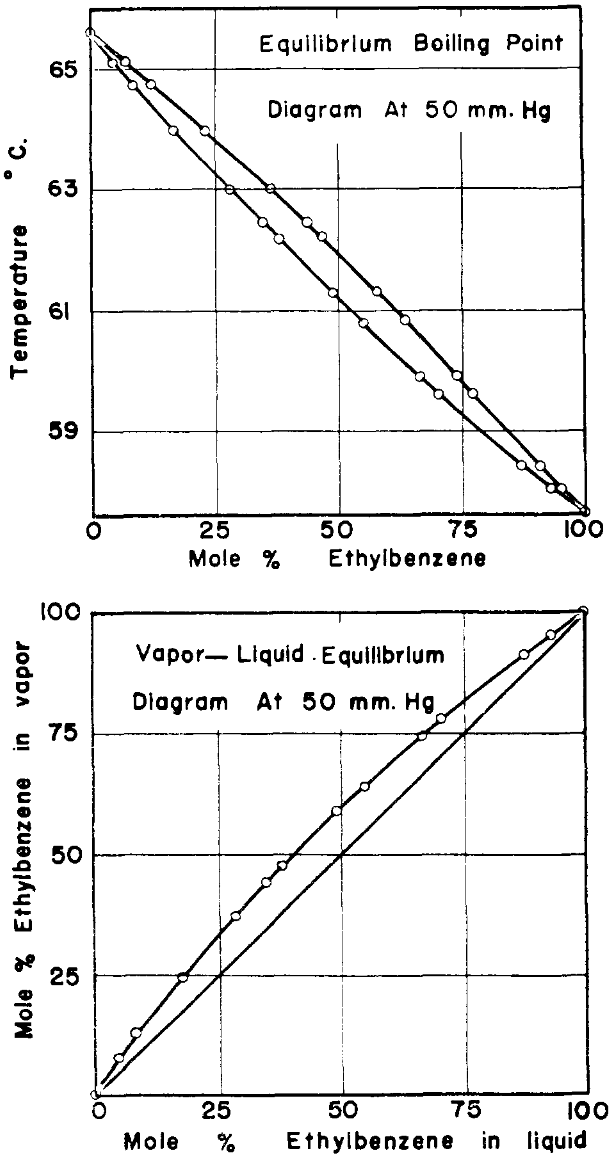

Figure 3. Ethylbenzene-styrene at 50 mm. of mercury

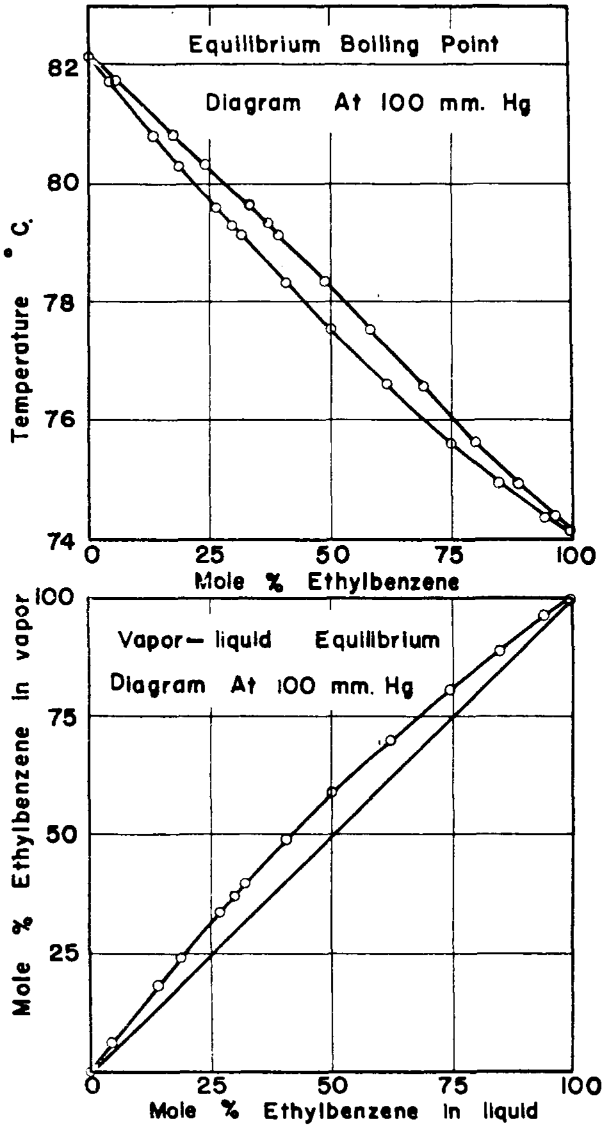

Figure 4. Ethylbenzene-styrene at 100 mm. of mercury

RESULTS

Vapor-liquid equilibrium data were obtained for the ethylbenzene-styrene system at pressures of 10, 20, 50, and 100 mm. of mercury and partial data were determined at 200 mm. of mercury. The fugacity coefficients for the system under investigation were found to be essentially unity. The experimental activity coefficients were also essentially unity over all pressures and temperatures tested and none of the several solutions of the Gibbs-Duhem equation satisfactorily correlated the data.

The experimental x-y data were plotted against temperature and the resulting plots were smoothed by drawing the best average curve through the points. The smoothed experimental data were used to calculate the total pressures and vapor compositions by means of Raoult's and Dalton's laws, assuming the experimental temperatures and liquid compositions to be correct. Table III includes the temperature, experimental data, smoothed experimental liquid and vapor composition data, and the calculated total pressure and vapor composition data. Smoothed experimental data are plotted as temperature vs. composition and as liquid composition vs. vapor composition in Figures 1 through 5.

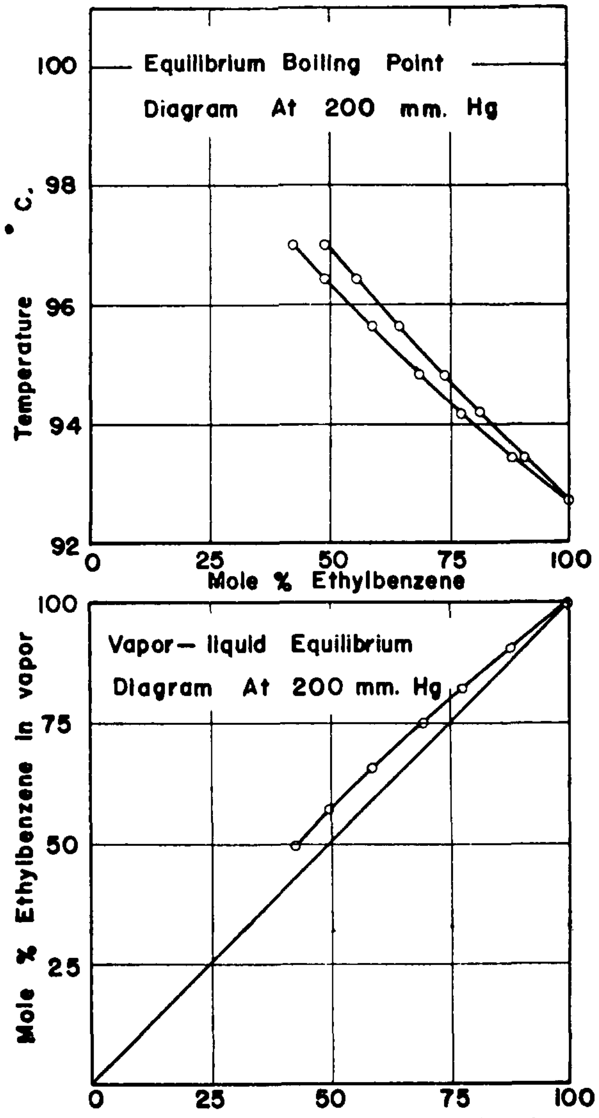

Figure 5. Ethylbenzene-styrene at 200 mm. of mercury

Only partial data could be determined at a pressure of 200 mm. of mercury because of the polymerization of styrene in mixtures containing more than 50 mole % of styrene at this condition.

The smoothed experimental data, obeying Raoult's law very closely, were found to have a maximum deviation in total pressure of 1.26% at 200 mm. of mercury, 1.11% at 100 mm. of mercury, 0.48% at 50 mm. of mercury, and 0.20% at 10 mm. of mercury. Judging from these results, the system is considered to be ideal over the whole range of investigation. The differences between the calculated vapor compositions and the experimental values were within the limit of experimental error and were of small magnitude. The over-all deviation from ideality as measured by the activity coefficients was found to be less than 2% over the whole range of investigation except for a few points at 200 mm. of mercury pressure.

The estimated possible errors of temperature, pressure, and concentration measurements were as follows:

Temperature ±0.1 °C.
Pressure ±0.5 mm. of mercury
Concentration ±0.001 mole fraction

NOMENCLATURE

P = vapor pressure of component at stated temperature
P_T = total pressure
t = temperature, °C.
T = temperature, °K.
x = mole fraction of component in liquid phase
y = mole fraction of component in vapor phase

Subscripts

1 = more volatile component (ethylbenzene)
2 = less volatile component (styrene)

LITERATURE CITED

(1) Boundy, R. H., Boyer, R. F., "Styrene, Its Polymers, Copolymers and Derivatives," p. 66, Reinhold, New York, 1952.

(2) Dreisbach, R. R., "Physical Properties of Chemical Substances," pp. 1.3, 2.1, Dow Chemical Co., Midland, Mich., 1952.

(3) Guttman, L., Westram, E. F., Jr., Pitzer, K. S., *J. Am. Chem. Soc.* **65**, 1246 (1943).

(4) Jones, C. A., Schoenburn, E. M., Colburn, A. P., *Ind. Eng. Chem.* **35**, 666 (1943).

(5) Patnode, W., Scheiber, W. J., *J. Am. Chem. Soc.* **61**, 3449 (1939).

(6) Perry, J. H., "Chemical Engineers' Handbook," 3rd ed., p. 163, McGraw-Hill, New York, 1950.

(7) Rasmussen, R. R., Van Winkle, M., *Ind. Eng. Chem.* **42**, 2121 (1950).

(8) Rossini, F. D., others, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," API Research Project 44, Carnegie Press, Pittsburgh, Pa., 1953.

(9) White, W. S., Van Winkle, M., *Ind. Eng. Chem.* **46**, 1284 (1954).

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