Part II

CHEMICAL ENGINEERING

INORGANIC CHEMISTRY

PHYSICAL CHEMISTRY

Vapor-Liquid Equilibrium Relations in Binary Systems

Ethylene–Chloroform System

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The vapor-liquid compositions and the molar volumes of the ethylene-chloroform system are presented at temperatures of 0°, 25°, 50°, 75°, and 100° C.

THIS STUDY represents work on one binary system in an over-all program designed to investigate *P-V-T-X* relations in binary hydrocarbon systems. The binary systems of normal paraffin series have been studied by many investigators. An excellent summary of work to 1950 on such systems was reported by Sage (*10*).

The olefin-paraffin group (ethylene–*n*-heptane) was studied by Kay (*4*) to obtain a comparison of the behavior of the system with that of the system ethane–*n*-heptane. Only small differences in phase behavior were observed between the two systems.

The volumetric behavior of pure ethylene was studied by several groups of investigators (*2, 7, 9*) and the properties of chloroform were measured in several studies (*3*).

EXPERIMENTAL

The apparatus used for this study was similar to that described by Kohn (*5*). The apparatus and experimental techniques were identical to those used in other recent studies of binary hydrocarbon systems (*6, 11*).

The ethylene was obtained from the Matheson Co. as "pure grade" material stated to contain 99.5% ethylene—impurities, ethane and carbon dioxide. A mass spectrometer test of the cylinder gas indicated a trace of ethane and air. The ethylene was passed through a silica gel drying tube and a steel bomb containing activated charcoal at 50 atm. pressure. The bomb was maintained at −40° C. in a bath of dry ice and acetone. The values of the pressure and temperature on the purified gas at the critical point—*i.e.*, at the disappearance of the meniscus—were 50.53 atm. and 9.54° C., respectively.

The chloroform (spectro quality reagent, Matheson Coleman Bell Co.) was de-aerated before each esperimental run and used without further purification.

RESULTS

Selected experimental bubble- and dew-point isotherms are presented in Figure 1. The average deviations of the data points for pressure, temperature, and mole fraction are ±0.10 atm., ±0.07° C., and ±0.004 mole fraction. The experimental data were smoothed by use of a large scale graph. Table I represents smoothed values of compositions and molar volumes of the coexisting gas and liquid phases at even values of pressure.

The values of dew-point compositions and molar volumes were not measured at 0° C. because of the difficulty of measuring accurately a few tenths of a mole per cent chloroform and because of the initial limited purity of the materials used. Since the dew-point states at 25° C. contain ethylene in excess of 0.99 mole fraction except at the very low pressures, the equilibrium properties at these states are regarded as identical to those of pure ethylene.

The phase behavior of this system is similar to that

Table I. Properties of the Coexisting Gas and Liquid Phases

	Bubble Point		Dew Point	
Press., Atm.	Mole fraction ethylene	Molar vol., ml./gram mole	Mole fraction ethylene	Molar vol., ml./gram mole
		0° C.		
10	0.236	70.8		
20	0.475	63.8		
30	0.708	59.6		
40	0.964	. . .		
		25° C.		
10	0.148	76.8	0.973	. . .
20	0.297	73.3	0.987	850
30	0.448	70.8	0.993	530
40	0.606	68.8	0.999	390
50	0.771	67.9	0.999[a]	. . .
60	0.968	. . .	0.978[a]	. . .
60.2[b]	0.969	133.3	0.969	133.3
		50° C.		
10	0.114	80.8	0.903	. . .
20	0.220	78.6	0.952	1550
30	0.324	76.5	0.966	655
40	0.431	74.5	0.970	565
50	0.539	72.7	0.972	525
60	0.654	71.7	0.972[a]	. . .
70	0.777	71.9	0.959[a]	. . .
76.8[b]	0.894	86.7	0.894	86.7
		75° C.		
10	0.078	84.2	0.828	. . .
20	0.164	82.6	0.905	1235
30	0.247	81.1	0.936	670
40	0.328	79.7	0.947	505
50	0.412	78.1	0.950	465
60	0.500	76.6	0.950	. . .
70	0.594	75.2	0.943[a]	. . .
80	0.694	74.7	0.926[a]	. . .
90	0.816	85.0	0.874[a]	. . .
90.9[b]	0.830	88.3	0.830	88.3
		100° C.		
10	0.057	88.1	0.658	. . .
20	0.124	86.5	0.833	. . .
30	0.192	84.9	0.870	815
40	0.260	83.5	0.886	565
50	0.327	82.2	0.896	462
60	0.398	80.9	0.902	410
70	0.479	79.5	0.904[a]	. . .
80	0.563	78.1	0.902[a]	. . .
90	0.654	77.6	0.888[a]	. . .
100	0.773	90.0	0.837[a]	. . .
100.9[b]	0.797	103.0	0.797	103.0

[a] Interpolated values. [b] Vapor-liquid critical points.

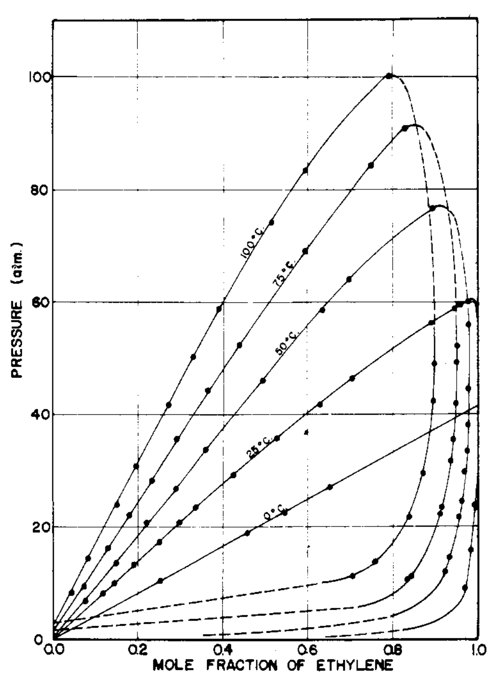

Figure 1. Selected experimental isotherms

of binary paraffin hydrocarbon systems, particularly the ethylene-n-heptane system (*4*).

Because of the anomalous behavior of pure ethylene at its critical point, described by McIntosh (*7*), the critical points of the ethylene–chloroform system were determined at four different isotherms. The qualitative critical behavior of the mixtures was not greatly different from that of pure ethylene. There was no sign of the formation of the sticky layer (a viscous complex), reported by Kay (*4*), and no attempt has been made to explain the difference. At pressures slightly lower than the critical pressure for each of the mixtures, the meniscus was sharp and flat, and no opalescence was noticeable except at the meniscus, which appeared brownish by trasmitted light. As the pressure was slowly increased, only a broad band of opalescence remained where a sharp meniscus was last seen. On heating, the opalescence decreased and gradually became uniform. The gas-liquid critical values at four isotherms are listed in the table. Due to the effects of "stirring" and the formation of a dispersion of liquid and vapor, the uncertainty in the critical volumes was as much as 20 cc./gram mole.

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