Heterogeneous-Phase Equilibrium in Ethylene–*n*-Dodecane System

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Vapor-liquid equilibrium compositions, pressures, and liquid molar volumes for the binary system of ethylene and *n*-dodecane are presented for four isotherms between 10° and 75°C. The Flory-Huggins model for liquid solutions is shown to fit the experimental data with considerably better accuracy than the Scatchard modification of regular solution theory.

In this work, accurate equilibrium data on the ethylene–*n*-dodecane system were obtained and used to test some of the simple solution models. There are no existing experimental data on this system, although several investigators have studied the equilibrium properties of ethylene with other normal paraffin solvents (*8*).

The pure components, ethylene and *n*-dodecane, have been studied by other groups of investigators (*4*, *7*, *9*, and *5*, *10*, respectively).

EXPERIMENTAL

The apparatus and experimental procedures have been described by Lee and Kohn (*6*). The basic apparatus consisted of a borosilicate glass equilibrium cell mounted in a constant temperature bath. Ethylene was transferred from a thermostated reservoir to the cell by a mercury displacement pump. The gas volumes delivered from the mercury displacement system to the equilibrium cell were measured to the nearest 0.006 ml. Pressures on the gas displacement reservoir and on the equilibrium cell were measured with Heise bourdon tube gages accurate to 0.07 atm. This accuracy was attained by frequent comparisons with the pressures taken on an Ashcroft dead weight gage. The Ashcroft gage had been calibrated against a Barnet dead weight gage which had been calibrated to 0.02% at the Meetinstituut BEMETEL TNO at Amsterdam. Bath temperatures were measured with a platinum resistance thermometer to 0.02°C. The platinum resistance thermometer had been calibrated by comparison to a calibration platinum resistance thermometer which had a certificate traceable to the NBS. Liquid volumes in the cell were read to 0.01 ml according to permanent calibration marks on the cell wall. The cells were calibrated with a macroburet.

The ethylene, obtained from the Matheson Company was CP grade stated to have 99.5% minimum purity. Vapor-liquid measurements of pressure as a function of quality upon the gas obtained directly from the cylinder at 7°C indicated pressure differences between the dew point and the bubble point of 0.4 atm. The measured critical temperature of the gas was 9.34°C at a critical pressure of 50.09 atm. These results would seem to indicate that the gas contained about 0.003 mole fraction of nitrogen. The *n*-dodecane was claimed by the supplier (Humphrey-Wilkinson, Inc.) to have 99.0% minimum purity. A freezing point on the *n*-dodecane was taken using a carefully calibrated platinum resistance thermometer. The air-saturated material had a sharply defined freezing point of −9.57°C. This is within 0.01°C of the value for *n*-dodecane reported by Rossini (*10*). Both the ethylene and the *n*-dodecane were used without further purification.

RESULTS

The smoothed values of the equilibrium pressures, compositions, and liquid molar volumes are listed in Table I. Four

Table I. Equilibrium Properties of Liquid Phase of Ethylene–*n*-Dodecane System

Press., atm	Mole fraction, ethylene	Molar vol, ml/g-mol
	10°C	
5.00	0.135	200.8
10.00	0.245	182.8
15.00	0.350	165.4
20.00	0.445	149.8
25.00	0.530	135.7
30.00	0.610	122.7
35.00	0.690	110.3
40.00	0.770	98.8
45.00	0.850	87.5
	25°C	
5.00	0.100	212.3
10.00	0.190	198.0
15.00	0.270	185.3
20.00	0.350	172.7
25.00	0.425	160.7
30.00	0.500	148.6
35.00	0.570	137.2
40.00	0.635	126.7
45.00	0.690	117.5
50.00	0.742	109.2
55.00	0.795	101.0
60.00	0.860	91.4
65.00	0.950	82.0
	50°C	
5.00	0.075	222.6
10.00	0.140	212.3
15.00	0.206	201.8
20.00	0.270	191.7
25.00	0.330	182.0
30.00	0.385	173.2
35.00	0.435	165.2
40.00	0.485	157.2
45.00	0.530	150.0
50.00	0.575	142.8
55.00	0.612	136.8
60.00	0.650	130.5
65.00	0.685	125.0
70.00	0.720	119.5
75.00	0.753	113.9
80.00	0.785	109.3
85.00	0.817	104.3
90.00	0.850	99.0

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Table I. *(Continued)*

Press., atm	Mole fraction, ethylene	Molar vol, ml/g-mol
	75°C	
5.00	0.065	230.7
10.00	0.120	221.7
15.00	0.170	213.7
20.00	0.220	205.3
25.00	0.265	198.0
30.00	0.310	190.8
35.00	0.353	183.7
40.00	0.395	177.0
45.00	0.435	170.5
50.00	0.475	164.0
55.00	9.510	158.2
60.00	0.542	152.8
65.00	0.575	147.2
70.00	0.602	142.5
75.00	0.632	137.2
80.00	0.660	132.7
85.00	0.685	128.2
90.00	0.712	123.5

bubble point isotherms were determined in the temperature range, 10–75°C. Each isotherm was obtained by several experimental runs to ensure reasonably good reproducibility. The average deviations of the experimental bubble points were ±0.10 atm, ±0.005 mole fraction of ethylene; for the liquid molar volume, it was ±1.0 ml/g-mol. Since the vapor pressure of *n*-dodecane is low (4.2 mm of Hg at 75°C), the vapor phase is virtually pure ethylene at all the temperatures and pressures studied. Extensive computations on the maximum amount of *n*-dodecane which could be in the gas phase generally showed that the mole fraction of *n*-dodecane in the gas phase was less than 0.002 mole fraction at pressures above 5 atm. Thus dew point isotherms were not measured.

The fugacities of ethylene in the liquid mixtures were treated computationally in the same manner as reported by Lee and Kohn (*6*) for the ethane–*n*-dodecane system. The smoothed composition data were fitted to both the Scatchard modification of regular solution theory (*11*) and the Flory-Huggins solution model (*1–3*). The characteristic energy parameters (ΔU_{12}) in both models were found to be approximately temperature independent in the temperature range studied. The energy parameter is 961 ± 34 cal/g-mol for the Flory-Huggins model and 469 ± 30 cal/g-mol for the Scatchard model. The standard deviation of the calculated ethylene fugacities from the 58 smoothed experimental values is 0.66 atm for the Flory-Huggins model and 1.22 atm for the Scatchard model.

Table II. Partial Molar Volumes at Infinite Dilution of Ethylene

(Ml./g-mol)

Temp, °C	Ethylene	*n*-Dodecane
10.0	61.0	223.0
25.0	63.5	227.0
50.0	68.0	234.0
75.0	71.8	240.5

Partial molar volumes of each of the components at infinite dilution of ethylene are tabulated in Table II. The partial molar volumes at each temperature are independent of composition within a few percent over the composition range covered in this study.

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Liquid-Vapor Equilibria and Thermodynamics of Lithium–Tin System

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As part of our study of binary liquid-metal systems containing an alkali metal, we have investigated the lithium-tin system at 1200°C. Previously, we reported data for the sodium-bismuth (*6*) and the sodium-lead (*5*) systems.

EXPERIMENTAL

The transpiration apparatus for the 1200°C experiments is shown in Figure 1 and is integrated with a helium atmosphere glovebox. The liquid metal sample is held in a long tantalum can, 10, which rests inside the 3-in. stainless steel furnace well, 8. A gas-tight seal is provided between the furnace well and the glovebox floor, 6, by means of a flange and O-ring protected from overheating by means of cooling coils (not shown). A similar gas-tight seal is provided between the cover plate, 5, and the glovebox floor. Three openings penetrate the cover plate. Two of these bear Veeco brand demountable connectors which permit gas-tight positioning of the tantalum thermocouple well, 11, and of the tantalum quench tube, 7. The third opening is the carrier gas inlet, 4. An additional Veeco

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