of viscosity given by the present correlation and the values computed by Dean and Stiel's (*3*)equations. This may be attributed to inherent errors in the method of determination of the pseudocritical constants (*3*). In Figure 1, a regular trend is noticed between the limits of the two pure components. This clearly brings out the effect of mixture composition on viscosity of the Freon-12–Freon-22 vapor mixture system.

CONCLUSION

The present correlation facilitates design of engineering systems, as viscosity information on pure Freon-12 and Freon-22 vapors and their mixtures may be obtained readily. The determination of viscosity, however, requires an accurate knowledge of the temperature-dependence of viscosity at zero density. For engineering purposes, it may be convenient to use the atmospheric viscosity values. These atmospheric viscosity values may be calculated for pure components by the correlation of Witzell and Johnson (*20*) and for mixtures by Herning and Zipperer's (*4*) equation or by Wilke's (*19*) equation.

NOMENCLATURE

a, b = coefficients in Table I
A, B = coefficients in Equation 1
A_m, B_m,
A_i, B_i = coefficients defined in Equations 2 & 3
M_i = molecular weight of the pure components
N = number of experimental points
P.E. = probable error
T = temperature
$\tilde{V}_m$ = molar volume of the mixture
$\tilde{V}_i$ = molar volume of the pure components
x_i = molar fractions of the pure components in the mixture
μ = viscosity at a given temperature and density
μ_0 = viscosity at the same temperature as μ but at zero density
$\bar{\mu}$ = viscosity as calculated from Equation 1
ρ = density
ρ_m = density of the mixture
σ = standard deviation

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Heterogeneous Phase Equilibrium in the Ethane–*n*-Dodecane System

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Vapor-liquid equilibrium compositions, pressures, and liquid molar volumes for the binary system of ethane and *n*-dodecane are presented for five isotherms between 0° and 100° C. The Flory-Huggins model of liquid solutions gave better results in fitting the experimental data than the Scatchard modification of regular solution theory.

THIS WORK was done to obtain accurate equilibrium data on the ethane–*n*-dodecane system and to test some of the simple solution models. The literature through 1967 shows no existing experimental data on this system. The ethane–*n*-octane system was reported recently by Rodrigues *et al.* (*16*).

The pure materials, ethane and *n*-dodecane, have been studied by many groups. The ethane has been studied extensively (*1–3, 13, 15, 17*) and the properties of *n*-dodecane were reported by several investigations (*8, 17*).

EXPERIMENTAL

The equipment and experimental techniques were described in detail by Kohn and Kurata (*11*) and were the same as those used in the previous studies of binary hydrocarbon systems (*9–11, 16–18, 20*). A complete schematic flow diagram of the apparatus is shown in Figure 1. The apparatus is mounted on a plywood housing with 1-inch, 90° steel flanges on the outside. The cell (*O*) temperatures were measured by a platinum resistance thermometer (*V*) and controlled by a Sargent Thermonitor proportional controller with probable error within ±0.02° C. The pressures were measured by Heise bourdon tube gages (*G*, *H*), with an accuracy of ±0.07 atm. The bourdon tube gages were checked frequently against an Ashcroft dead weight gage (*S*). The equilibrium cell (*O*) used in this study was a 10-ml. borosilicate glass cell and of the same type as those used in the earlier works.

The equilibrium cell was initially partially filled with a known amount of liquid *n*-dodecane. The weight was

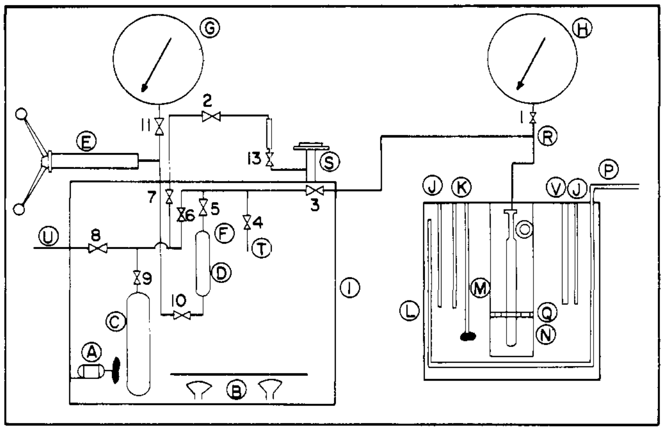

Figure 1. Flow diagram of apparatus

determined to the nearest milligram by use of an analytical balance. The cell was then purged free of air by flushing with ethane gas. The compositions of ethane in the liquid solutions were determined from the stoichiometric analysis of the amount of the pure ethane which was added to the cell from a reservoir (*D*) by a manually operated mercury displacement pump (*E*). The gas in the reservoir was kept at a constant pressure of 41.81 atm. during 0° and 25° C. isothermal runs and 62.22 atm. during the higher temperature isothermal runs. Its temperature was also kept constant during each run at around 62° C., with probable error ±0.07°. The mercury displacement pump has an accuracy of ±0.01 ml. The temperature of the delivery line was kept at 60° C. with probable error of ±2°, and its volume was calibrated as a function of pressure at that temperature. Its volume was around 0.9 ml.

The ethane used in this study was the same grade and was prepurified the same as the ethane used in the previous study (*12, 16*). It was thought to be 99.7 mole % ethane. The *n*-dodecane was claimed by the supplier (Humprey-Wilkinson, Inc.) to be at least 99.0 mole % pure. It had a refractive index of 1.4220 at 20° C., which was in good agreement with the literature value 1.4216 (*17*). It was used as received without further purification. The impurities are believed to be paraffinic hydrocarbons of similar molecular weight.

RESULTS

Figure 2 presents equilibrium pressure *vs.* mole fraction ethane in the liquid phase. Five bubble point isotherms were determined in the temperature range from 0° to 100° C. and at pressures up to 62 atm. Each isotherm was obtained by several experimental runs to get a reasonably good reproducibility. The average deviations of the experimental bubble points were ±0.09 atm. and ±0.0019 mole fraction of ethane. Since the vapor pressure of the *n*-dodecane is very low (15.0 mm. of Hg at 100° C.), the vapor phase was considered as pure ethane, and dew-point isotherms were not measured separately in this work.

Figure 3 presents the curves of liquid molar volume *vs.* mole fraction ethane in the saturated liquid phases. The average deviations of the experimental runs were ±0.79 ml. per gram mole and ±0.0025 mole fraction of ethane. The smoothed values of the equilibrium properties are given in Table I. The fugacities of ethane are also tabulated in Table I. The vapor phase is almost pure ethane in the temperature range of this study. Therefore, the compressibility factors of pure ethane (*13*) were used in the calculations of the ethane fugacities. Graphical integrations were applied in these calculations.

The fugacities of ethane along each isotherm were fitted to both the Scatchard (*19*) modification of regular solution

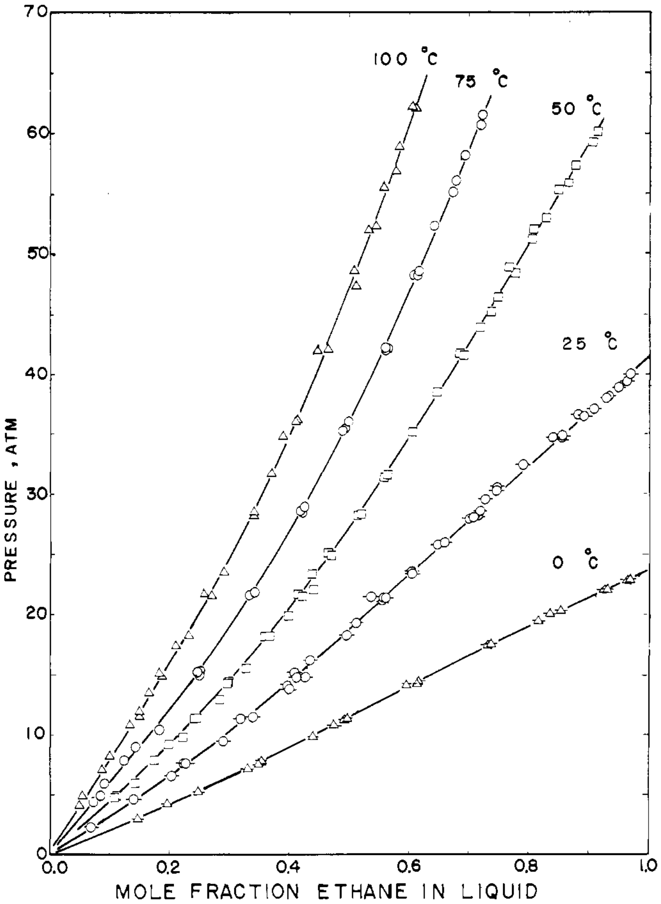

Figure 2. Pressure *vs.* mole fraction ethane in the liquid phase

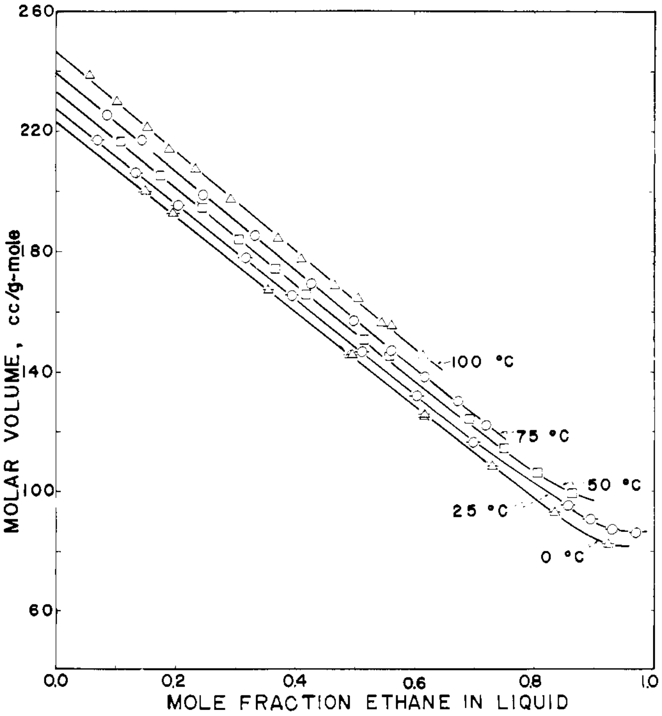

Figure 3. Molar volume–composition diagram

Table I. Equilibrium Properties of the Liquid Phase of the Ethane–*n*-dodecane System

Pressure, Atm.	Mole Fraction	Molar Volume, Ml./ Gram Mole	Ethane Fugacity Atm.
0° C.			
4.00	0.190	193.0	3.83
8.00	0.365	165.5	7.33
12.00	0.522	140.8	10.52
16.00	0.677	116.9	13.40
20.00	0.843	92.4	15.98
22.00	0.935	80.9	17.14
			$\sigma_F = 0.615$ $\sigma_S = 0.659$
25° C.			
4.00	0.125	208.5	3.88
8.00	0.240	190.3	7.51
12.00	0.345	173.9	10.91
16.00	0.440	158.8	14.07
20.00	0.530	144.8	16.99
24.00	0.614	131.4	19.68
28.00	0.700	117.9	22.13
32.00	0.790	104.0	24.34
36.00	0.882	91.9	26.29
40.00	0.980	86.0	27.94
			$\sigma_F = 0.605$ $\sigma_S = 0.795$
50° C.			
4.00	0.088	219.4	3.91
8.00	0.174	205.5	7.64
12.00	0.254	192.5	11.18
16.00	0.327	180.6	14.54
20.00	0.393	170.0	17.71
24.00	0.454	160.0	20.71
28.00	0.512	150.9	23.53
32.00	0.565	142.1	26.17
36.00	0.616	131.6	28.64
40.00	0.666	126.9	30.93
44.00	0.715	119.5	33.03
48.00	0.764	112.5	34.95
52.00	0.813	105.8	36.70
56.00	0.861	100.2	38.24
60.00	0.910	95.4	39.58
62.00	0.936	93.1	40.20
			$\sigma_F = 1.047$ $\sigma_S = 1.420$
75° C.			
4.00	0.068	229.0	3.93
8.00	0.129	219.0	7.71
12.00	0.198	207.7	11.35
16.00	0.259	197.7	14.85
20.00	0.314	188.6	18.20
24.00	0.365	180.4	21.42
28.00	0.414	172.4	24.50
32.00	0.458	165.2	27.44
36.00	0.498	158.7	30.25
40.00	0.536	152.5	32.92
44.00	0.578	145.4	35.46
48.00	0.608	140.8	37.88
52.00	0.644	135.8	40.16
56.00	0.676	130.3	42.31
60.00	0.710	125.2	44.34
62.00	0.727	122.8	45.31
			$\sigma_F = 1.059$ $\sigma_S = 1.468$
100° C.			
4.0	0.050	238.4	3.92
8.0	0.101	230.0	7.75
12.0	0.152	221.6	11.46
16.0	0.200	213.7	15.10
20.0	0.247	206.0	18.59
24.0	0.292	198.6	21.97
28.0	0.334	191.6	25.24
32.0	0.373	185.2	28.40
36.0	0.409	179.2	31.45
40.0	0.444	173.5	34.39
44.0	0.475	168.5	37.23
48.0	0.506	163.2	39.98
52.0	0.536	158.2	42.62
56.0	0.565	153.5	45.17
60.0	0.594	148.8	47.62
62.0	0.608	146.4	48.81
			$\sigma_F = 0.839$ $\sigma_S = 0.938$

theory and the Flory-Huggins (*4*, *5*, *7*) solution model. Each model has a single parameter, i.e., interchange energy parameter. The expressions for the component fugacity for these models are for the Scatchard modification of regular solution theory,

$$f_1 = f_1^\circ\, x_1 \exp\left\{\frac{\Delta u_{12}}{RT}\left(\frac{\bar{V}_1}{\bar{V}_2}\right)^{1/2} \phi_2^2\right\} \tag{1}$$

while for the Flory-Huggins model,

$$f_1 = f_1^\circ\, \phi_1 \exp\left\{\phi_2\left(1 - \frac{\bar{V}_1}{\bar{V}_2}\right) + \frac{\Delta u_{12}}{RT}\left(\frac{\bar{V}_1}{\bar{V}_2}\right)^{1/2} \phi_2^2\right\} \tag{2}$$

where

$$\phi_1 = \frac{x_1 \bar{V}_1}{x_1 \bar{V}_1 + x_2 \bar{V}_2} \quad \text{and} \quad \phi_2 = \frac{x_2 \bar{V}_2}{x_1 \bar{V}_1 + x_2 \bar{V}_2}$$

The standard state fugacity (f_1°) is the fugacity of the hypothetically pure incompressible liquid ethane at the temperature and pressure of the system. It was computed from the following equation

$$f_1^\circ \Big|_{(P,T)} = P_1^\circ \frac{f}{P} \Big|_{(P_1^\circ,T)} \exp\left\{\frac{\bar{V}_1}{RT}(P - P_1^\circ\right\} \tag{3}$$

where P_1° is the vapor pressure of component 1 at the temperature of the system, T, and $\bar{V}_1$ is the partial molar volume of ethane in a dilute solution at temperature T.

Above the critical temperature of ethane, its vapor pressure was extrapolated using a modification of an equation proposed by Hougen *et al.* (*6*):

$$\log P_r^\circ = \frac{-A(1 - T_r)}{T_r} \tag{4}$$

where the constant $A = 2.5693$ was computed from the normal boiling point of ethane.

The fugacity coefficients

$$\frac{f}{P}\Big|_{(P_1^\circ,T)}$$

were obtained by the use of Pitzer's three-parameter method (*14*). The partial molar volumes of the components used in the above equations were obtained from the molar volume data (Figure 3). The figure shows that the molar volume *vs.* ethane concentration lines are linear in low concentration ranges, but in the concentrated regions deviate considerably from linearity. The partial molar volume of each component was determined by the intercepts of the straight lines which

Table II. Partial Molar Volumes (Ml./Gram Mole)

Temp., ° C.	Ethane	*n*-Dodecane
0.0	65.8	222.2
25.0	69.9	227.4
50.0	74.2	231.4
75.0	77.7	239.0
100.0	82.2	246.8

were drawn by the least square fit of the data in the low concentration ranges (mole fraction of the ethane less than 0.7). The partial molar volumes for each component are tabulated in Table II.

Through the use of the smoothed experimental data in Table I and the standard state fugacities defined by Equation 3, the values of the interchange energy Δu_{12} were computed at each pressure in every isotherm for both solution models. These energy parameters calculated from the Flory-Huggins model were very approximately constant in all isotherms and through the pressure ranges studied except at high concentration regions. Large deviations in the high concentration ranges could be expected, since the molar volume *vs.* ethane mole fraction curves deviate considerably from linearity in these regions. The interchange energies computed for the Scatchard model were considerably more scattered than the values from the Flory-Huggins model. But the over-all results showed that the interchange energy parameters for both models could be considered as constants for all practical purposes in the temperature range of 0° to 100° C. The best constants were obtained by a least squares program for all data points except the high-concentration regions. The results were 849 cal. per gram mole with a standard deviation of 70 cal. per gram mole for the Flory-Huggins model, and 414 cal. per gram mole with standard deviation of 102 cal. per gram mole for the Scatchard model. The fugacities of the ethane in the liquid phase were calculated from both models, using the best constants for the interchange energy parameters. The standard deviations of the calculated fugacities from the experimental values are listed in the Table I for each isotherm. The standard deviations calculated from all values were 0.91 atm. for the Flory-Huggins model and 1.20 atm. for the Scatchard model. But if the values in the high-pressure regions were excluded, the standard deviations are considerably reduced. The standard deviations of all values up to 44 atm. are 0.54 atm. for the Flory-Huggins model and 0.76 for the Scatchard model. These values are slightly greater than those obtained from the ethane–*n*-octane system in the previous work. However, the Flory-Huggins model is accurate enough to represent the deviations of this system from Raoult's law for most engineering purposes even at the elevated pressures.

NOMENCLATURE

f_i = fugacity of component i in atm.; $i = 1,2$
f_i° = standard state fugacity of component i in atm.; $i = 1,2$
R = universal gas law constant = 1.987 cal. per gram mole ° K.
T = temperature in ° K.
T_r = reduced temperature, T/T_c
Δu_{12} = interchange energy for component 1 and 2 in cal. per gram mole
$\bar{V}_i$ = partial molar volume of component i in the liquid solution in ml./g. mole; $i = 1,2$
X_i = mole fraction of component i in the liquid; $i = 1,2$
ϕ_i = liquid volume fraction of component i; $i = 1,2$
σ = standard deviation of the calculated ethane fugacities from the experimental values

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