Table II. Zero-Pressure Refractivity of *i*-Butane

Temp, °F	R_{LL}^0, cc/g mol
100	20.64
160	20.72
220	20.78
250	20.82

These values were calculated by using the measured refractive indices of pure *i*-butane together with the volumetric data reported by Sage and Lacey (*3*).

Discussion

No comparison is made between the experimental results obtained in this work and those of other workers, because no previous investigation of this binary system is reported in the literature.

Although the refractive indices of the phases can be measured with high accuracy, there are some limitations to the accuracy of the calculated densities. These limitations are caused by the slight variation of the Lorentz-Lorenz molar refractivity with density for both pure components and mixtures and also by the existence of minor nonadditive terms. In general, these limitations seldom cause inaccuracies greater than 1 or 2% in the calculated density. When results of higher precision are required, the nature and magnitude of the variation of the refractivity with density and composition must be determined by some independent density measurements.

Nomenclature

K_{CO_2} = equilibrium ratio for carbon dioxide
$K_{i\text{-}C_4}$ = equilibrium ratio for *i*-butane
M = molecular weight
n = refractive index
n_L = refractive index of liquid
n_V = refractive index of vapor
P = pressure, psia
R_{LL} = Lorentz-Lorenz molar refractivity, cc/g mol
R_{LL}^0 = zero-pressure Lorentz-Lorenz refractivity
V_L = molar volume of liquid
V_V = molar volume of vapor
x = mole fraction of a component in the liquid phase
y = mole fraction of a component in the vapor stage
ρ = density

Literature Cited

(1) Besserer, G. J., Robinson, D. B., *Can. J. Chem. Eng.*, **49** (5), 651 (1971).
(2) Kielich, S., *Physica*, **28**, 1116 (1962).
(3) Sage, B. H., Lacey, W. N., *Ind. Eng. Chem.*, **30** (6), 673 (1938).
(4) Smyth, C. P., Engel, E. W., Wilson, Jr., E. B., *J. Amer. Chem. Soc.*, **51**, 1736 (1929).
(5) Stoll, E., *Ann. Phys.*, **69**, 81 (1922).

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Equilibrium-Phase Properties of *i*-Butane–Ethane System

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Vapor and liquid equilibrium-phase compositions and refractive indices were determined for the *i*-butane–ethane system at 100.6°, 160.4°, 219.7°, and 249.6°F from the vapor pressure of *i*-butane to pressures in the critical region for the system. An analysis of data reported earlier on this system at temperatures of 32°, −4°, −40°, −76°, and −94°F indicates the possibility of significant errors, particularly in the vapor-phase data at the lower three temperatures.

Ethane and *i*-butane are present in essentially all multicomponent mixtures of interest to the petroleum and natural gas processing industry. The only previous work reported in the literature on the phase behavior of this binary system is that of Skripa et al. (4) who reported five isotherms in the region from 0° to −70°C. This work includes higher temperatures in the region from 100° to 250°F. This study is a continuation of the program referred to in an earlier paper (2) and includes experimental measurements of the phase compositions and refractive indices of the coexisting phases.

Experimental

The equipment described earlier by Besserer and Robinson (*1*, *2*) was used without further modification for the present study. Experiments were carried out at each of four temperatures which were nominally 100°, 160°, 220°, and 250°F. At each temperature, measurements were made at a series of pressures between the vapor pressure of *i*-butane and the critical pressure for the system.

The *i*-butane was instrument grade purchased from the Matheson Co. The ethane was research grade supplied by the Phillips Petroleum Co. In both cases, analysis showed the materials to be greater than 99.9 mol % pure.

The analytical procedures were the same as those reported earlier (2). The column was ⅛-in. diameter stainless-steel, 6-ft long filled with Poropak Q. The oven temperature was 100°C. The thermal conductivity cell detector was maintained at 200°C with a filament current of 150 mA at a helium flow rate of 25 cc/min. The chromatograph was calibrated by use of pure components, and area fractions were converted to mole fractions by multiplying the area of the ethane peak by 1.5110 and the area of the *i*-butane peak by 1.000.

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Results

The experimental measurements of the equilibrium-phase compositions and refractive indices, together with the calculated phase densities and vapor-liquid equilibrium ratios for both components, are given in Table I. The vapor and liquid-phase envelopes at each of the four temperatures of 100.6°, 160.4°, 219.7°, and 249.6°F are shown as a function of pressure and composition in Figure 1. Figures 2, 3, and 4 show the refractive indices, the calculated phase densities, and the equilibrium ratios, respectively, for both ethane and *i*-butane.

The phase densities were calculated from the phase compositions and refractive indices by use of the Lorentz-Lorenz molar refractivity relationship described previously (*2*) and by assuming that the refractivities are additive. The molar refractivity for ethane was taken from the work of Sliwinski (*5*) and was essentially constant at a value of 11.23 cc/g mol at the conditions of interest. The molar refractivity for *i*-butane was obtained from the relation:

$$R_{LL} = R_{LL}^0 - 6.9(10^{-5})P$$

and the table of R_{LL}^0 values given earlier (*2*).

Table I. Experimental Equilibrium-Phase Properties for *i*-Butane–Ethane System

				100.6°F				
Press, psia	Composition[a]		Refractive index[b]		Molar vol[c]		Equilibrium constant	
	Liquid	Vapor	Liquid	Vapor	Liquid	Vapor	Ethane	*i*-Butane
73	0.000	0.000	1.3063	1.00696	1.750	...	...	1.000
155	0.1782	0.5524	1.29515	1.01137	1.649	32.68	3.100	0.5447
207	0.2742	0.6863	1.28789	1.01418	1.606	24.08	2.503	0.4322
219	0.2951	...	1.28616	...	1.598	...	...	...
326	0.4841	0.8277	1.26889	1.02225	1.524	13.92	1.710	0.3340
334	0.4978	...	1.26747	...	1.519	...	...	...
401	0.5955	0.8639	1.25551	1.02842	1.494	10.63	1.451	0.3365
449	0.6648	0.8879	1.24521	1.03306	1.485	8.977	1.336	0.3344
516	0.7536	0.9152	1.23012	1.04032	1.485	7.218	1.214	0.3442
584	0.8314	0.9267	1.21232	1.05041	1.516	5.686	1.127	0.3761
585	0.8318	0.9370	1.21247	1.04949	1.514	5.590	1.127	0.375
636	0.8858	0.9481	1.19536	1.05938	1.576	4.792	1.071	0.4529
639	0.8875	0.9524	1.19484	1.06075	1.577	4.669	1.072	0.423
664	0.9135	0.9588	1.18652	...	1.611	...	1.050	0.4763
712	0.9541	0.9788	1.16210	1.08755	1.785	3.188	1.026	0.4619
723	0.9626	...	1.15736	...	1.825	...	...	...
				160.4°F				
P	*x*	*y*	n_L	n_V	V_L	V_V	K_{C_2}	$K_{i\text{-}C_4}$
170	0.000	0.000	1.2774	1.01581	1.930	...	...	1.000
191	0.0367	0.1771	1.27364	1.01750	1.899	26.20	4.826	0.8543
224	0.0867	0.2999	1.27060	1.01954	1.876	22.04	3.459	0.7666
289	0.1697	0.4513	1.26309	1.02372	1.847	16.71	2.659	0.6609
336	0.2328	0.5330	1.25712	1.02704	1.827	13.97	2.290	0.6087
418	0.3285	0.6201	1.24638	1.03349	1.808	10.70	1.888	0.5657
513	0.4333	0.6962	1.23282	1.04181	1.799	8.164	1.607	0.5361
569	0.4931	0.1194	1.22414	1.04860	1.801	6.922	1.459	0.5536
608	0.5366	0.7382	1.21672	...	1.811	...	1.376	0.5650
693	0.6240	0.7766	1.19654	1.06721	1.908	4.827	1.225	0.6104
779	0.7118	0.7792	1.16279	1.09324	2.127	3.491	1.095	0.7661
				219.7°F				
327	0.000	0.000	1.2368	1.03467	2.220	...	...	1.000
340	0.0226	0.0593	1.23535	1.03640	2.206	13.42	2.624	0.9625
394	0.0812	0.1827	1.22958	1.04049	2.195	11.37	2.250	0.8895
441	0.1345	0.2657	1.22281	1.04583	2.201	9.631	1.975	0.8582
489	0.1638	0.3342	1.21691	1.05073	2.225	8.396	2.040	0.7962
532	0.2269	0.3854	1.20801	1.05552	2.242	7.465	1.699	0.7950
602	0.2742	0.4048	1.20034	1.06728	2.267	6.106	1.476	0.820
657	0.3421	0.4554	1.18770	1.07972	2.326	5.019	1.333	0.827
701	0.3811	0.4694	1.16936	1.09690	2.512	4.109	1.232	0.858
720	0.4169	0.4690	1.14289	1.11448	2.901	3.492	1.124	0.910
				249.6°F				
438	0.000	0.000	1.2110	1.05744	2.520	...	...	1.000
464	0.211	0.0431	1.20680	1.05702	2.498	8.676	2.043	0.9775
493	0.0583	0.1153	1.19938	1.06390	2.541	7.488	1.978	0.9395
545	0.1183	0.2031	...	...	...	...	1.717	0.9038
574	0.1372	0.2082	1.18525	1.08420	2.623	5.447	1.517	0.9177
607	0.1672	0.2197	...	1.09064	...	5.037	1.314	0.9370

[a] Mole fraction ethane. [b] Relative to vacuum at 6328 Å. [c] Ft³/lb mol calculated from the refractive index and composition data.

Discussion

The calculated equilibrium ratios and the experimental vapor and liquid-phase envelopes obtained from this work and the work of Skripa et al. (*4*) were compared with the values predicted by the correlation of Prausnitz and Chueh (*3*). For making these predictions, a value of k_{12} equal to zero was used. The equation for the Henry's constant was

$$\ln H_{2(1)}{}^0 = -168.67277 + 408.43945\,\beta - 352.60010\,\beta^2 + 134.17229\,\beta^3 - 19.09930\,\beta^4 \quad (1)$$

where $\beta = 1000/T$. The equation for the $\alpha_{2(1)}$ values was

$$\alpha_{2(1)}{}^{1/2} = -6.22361 + 8.55244\,\theta - 4.11572\,\theta^2 + 0.93902\,\theta^3 - 0.10434\,\theta^4 + 0.00460\,\theta^5 \quad (2)$$

where $\theta = T/100$.

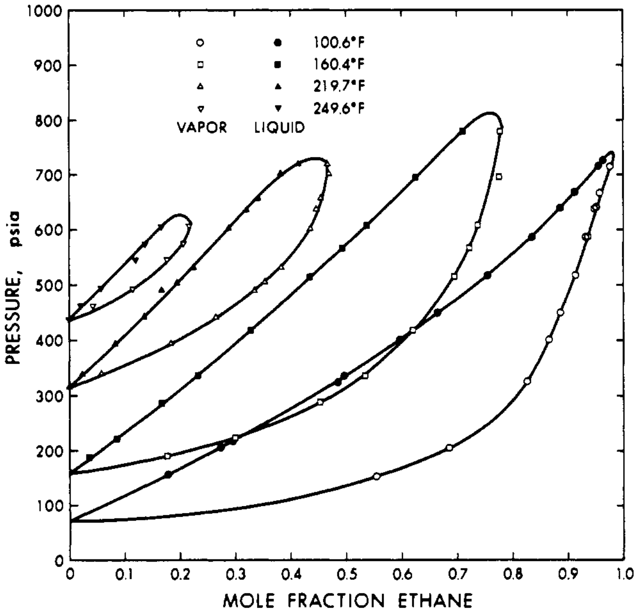

Figure 1. Pressure-equilibrium phase composition diagram for *i*-butane-ethane system

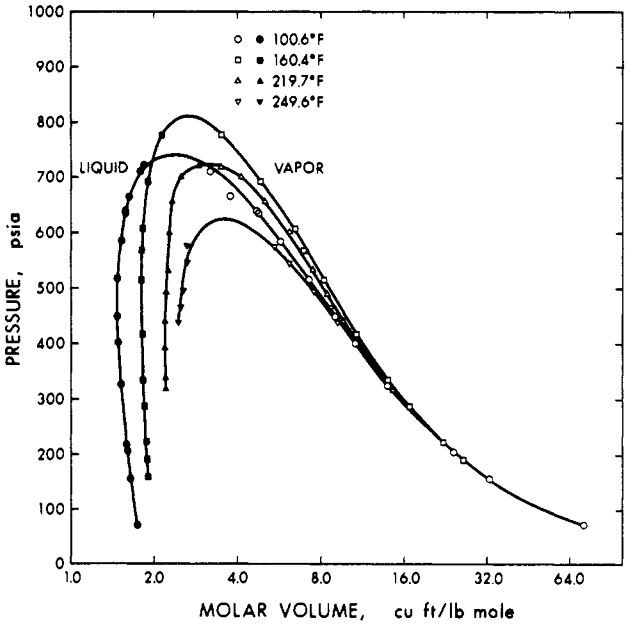

Figure 3. Pressure-equilibrium phase molar volume diagram for *i*-butane-ethane system

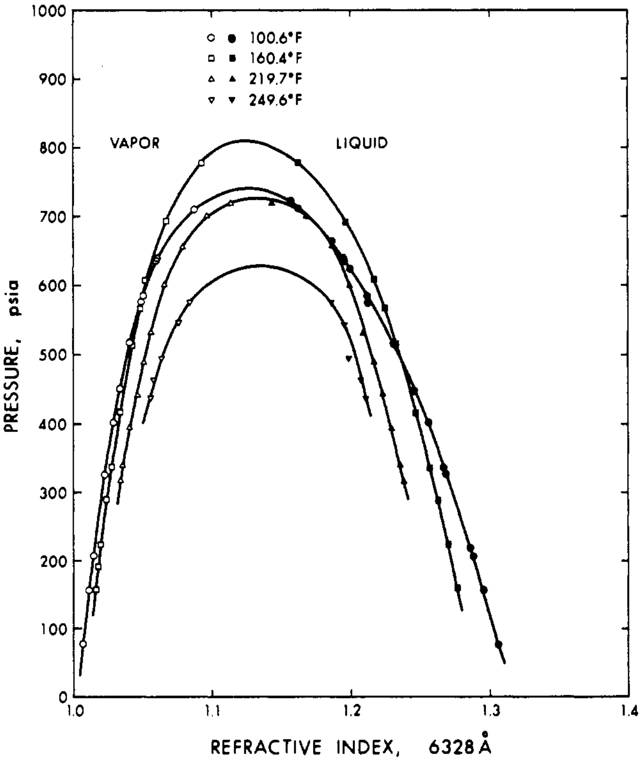

Figure 2. Pressure-equilibrium phase refractive index diagram for *i*-butane-ethane system

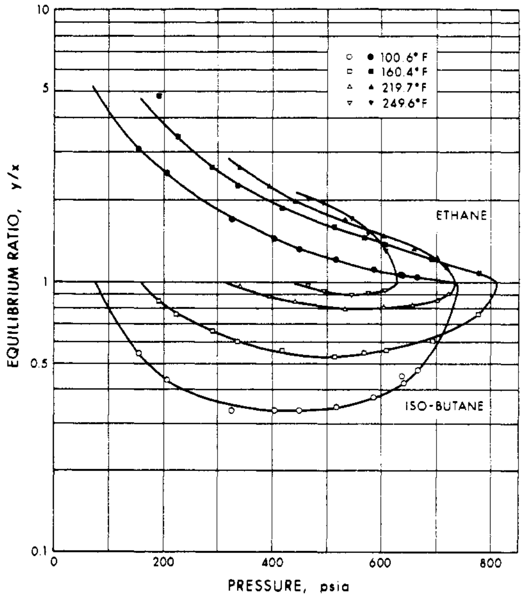

Figure 4. Equilibrium ratios for *i*-butane and ethane in *i*-butane-ethane binary system

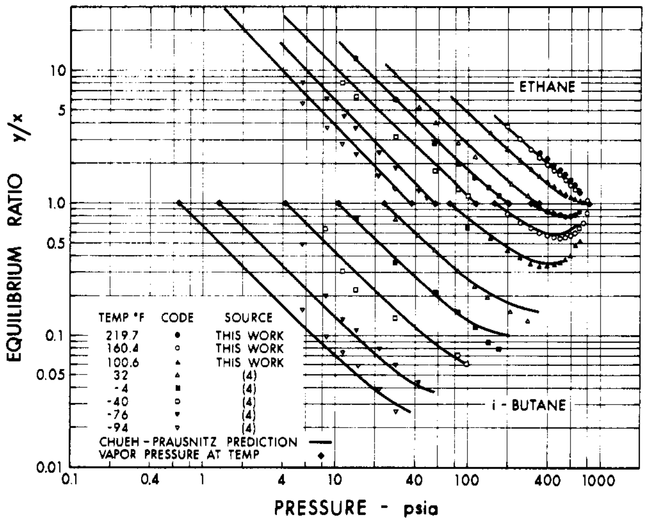

Figure 5. Comparison of predicted and experimental equilibrium ratios for *i*-butane and ethane in *i*-butane–ethane binary system

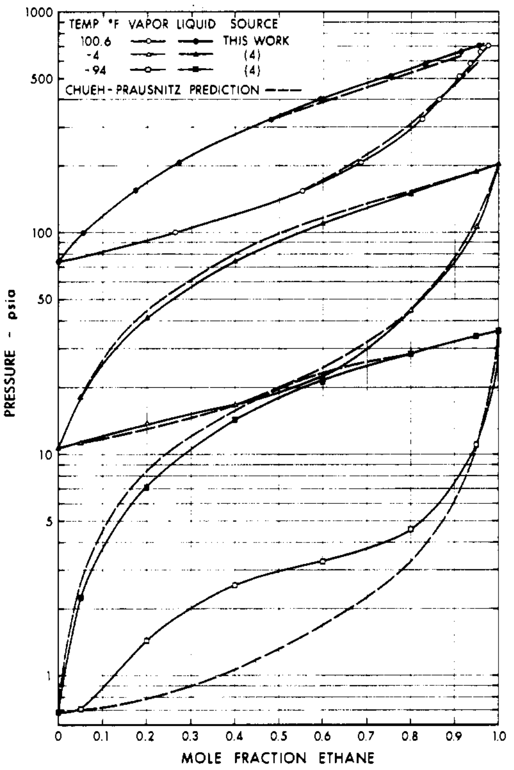

Figure 6. Experimental and predicted pressure-composition relationships for *i*-butane-ethane system

The points on Figure 5 illustrate the experimental equilibrium ratios, and the smooth curves represent the predictions from the Prausnitz correlation. The scatter of the data about the predicted curve indicates the possibility of some inconsistencies in the data.

The phase envelopes shown in Figure 6 show more clearly the regions where the experimental data may be open to question. The generally good agreement between the experimental and predicted results shown on the figure for the 100°F isotherm is typical for all isotherms at 32°F and above. The −4°F isotherm is typical of the −40°F isotherm as well, where the experimental data tend to be above the predicted values for the vapor phase at low ethane concentrations and below the predicted values at higher ethane concentrations. The −94°F isotherm is similar to the −76°F isotherm where all of the experimental data for the vapor phase are significantly above the predicted curve. The generally sigmoidal nature of the saturated vapor curves shown for all isotherms between −4° and −94°F is not typical for binary vapor-liquid equilibrium in hydrocarbon systems and suggests substantial errors in the data, particularly at the lower two or three temperatures.

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Nomenclature

$\alpha_{2(1)}$ = self-interaction constant for ethane in *i*-butane
β = temperature function in equation for Henry's constant
$H_{2(1)}{}^0$ = Henry's constant for ethane in *i*-butane at zero pressure
k_{12} = binary interaction constant
K = equilibrium ratio
K_{C_2} = equilibrium ratio for ethane
$K_{i\text{-}C_4}$ = equilibrium ratio for *i*-butane
n_L = refractive index of liquid
n_V = refractive index of vapor
P = pressure, psia
R_{LL} = Lorentz-Lorenz molar refractivity, cc/g mol
$R_{LL}{}^0$ = zero-pressure Lorentz-Lorenz molar refractivity, cc/g mol
θ = temperature function in equation for $\alpha_{2(1)}$
T = temperature, °R
x = mole fraction of a component in the liquid phase
y = mole fraction of a component in the vapor phase
V_L = molar volume of liquid, ft^3/lb mol
V_V = molar volume of vapor, ft^3/lb mol

Literature Cited

(1) Besserer, G. J., Robinson, D. B., *Can. J. Chem. Eng.*, **49**, 651 (1971).
(2) Besserer, G. J., Robinson, D. B., *J. Chem. Eng. Data*, **18**, 298 (1973).
(3) Prausnitz, J. M., Chueh, P. L., "Computer Calculations for High-Pressure Vapor-Liquid Equilibria," Prentice-Hall, Englewood Cliffs, N.J., 1968.
(4) Skripa, V. G., Nikitina, I. E., Zhdanovich, L. A., Sicotin, A. G., Benyaminovich, O. A., *Gazov. Prom.*, **15** (12), 35 (1970).
(5) Sliwinski, P., *Z. Phys. Chem., Neve Folge*, **63**, 263 (1969).

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