are given in Tables III and IV for the nitrobenzene–n-pentane and the nitrobenzene–n-heptane systems, respectively. These data were fitted to the following equation

$$\Delta\eta = \left(\frac{A}{\alpha}\right)(\epsilon^{-\alpha} - 1) + B \qquad (2)$$

where ϵ is $(T - T_c)/T_c$ and T_c is the critical temperature. Fisher (4) pointed out that a value of α in $-1 < \alpha < 0$ gives a cusp, $\alpha = 0$ a logarithmic divergence, and that in $\alpha > 0$ a power-law divergence. The fitted parameters are: for nitrobenzene–n-pentane, $A = 0.0594 \pm 0.0114$, $B = -0.182 \pm 0.008$, $\alpha = -0.154 \pm 0.051$, for $3.4 \times 10^{-6} < \epsilon < 10^{-2}$; and for nitrobenzene–$n$-heptane, $A = 0.0859 \pm 0.0123$, $B = -0.273 \pm 0.019$, $\alpha = -0.135 \pm 0.039$, for $3.4 \times 10^{-6} < \epsilon < 10^{-2}$. The values of the exponent are of the same order for these two systems, and they are both negative. The values are close to those obtained by Allegra et al. (1) for the isobutyric acid–water system. The present results seem to support the prediction of Kadanoff–Swift that the singularities of the viscosity at the critical point lead to a cusp rather than an infinity.

Glossary

t	temperature, °C
t_c	critical temperature, °C
T	temperature, K
T_c	critical temperature, K
T_s	phase-separation temperature, K
x_{NB}	mole fraction of nitrobenzene
$x_{NB,c}$	mole fraction of nitrobenzene of critical mixture
ϵ	$(T - T_c)/T_c$
η	viscosity, cP
η^0	ideal viscosity, cP
$\Delta\eta$	excess viscosity, cP
ρ	density, g cm^{-3}

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The Equilibrium Phase Properties of the Nitrogen–Isopentane System

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Vapor and liquid equilibrium phase compositions and refractive indices have been determined for the nitrogen–isopentane system at 40.0, 99.8, 159.8, and 219.6 °F from the vapor pressure of isopentane to about 3000 psia. The equilibrium ratios for each component were calculated at each temperature from the phase composition data. The equilibrium phase densities were calculated from the measured phase compositions and refractive indices using the Lorentz–Lorenz molar refractivity relationship.

Nitrogen is frequently present in natural gas and related fluids and consequently its presence must be recognized when determining the thermodynamic properties of these multicomponent systems. As in the case of other nonhydrocarbon components, the binary interaction parameters between nitrogen and paraffin hydrocarbons are normally not small enough to be neglected. One way of obtaining these parameters is by using experimental data obtained by measuring equilibrium phase compositions. The object of the work undertaken in this study was to obtain phase behavior data on mixtures of nitrogen and isopentane at pressures up to about 3000 psia and over a temperature range from about 40 to 220 °F. As far as could be determined, no previous studies have been reported on this system.

Experimental Method

The experimental method used in this work was essentially the same as that used in several earlier studies on other systems. This was described in detail in papers by Besserer and Robinson (2, 3) and more recently by Kalra et al. (8). The equilibrium cell was of the variable volume type with provision for sampling both liquid and vapor phases at equilibrium and for determining the refractive index of each phase.

The system temperature was measured with a calibrated iron–constantan thermocouple relative to an ice junction such that the temperature is believed known to ±0.1 °F. The pressure was measured with a calibrated 0–3000 psi Heise gauge equipped with a type 316 stainless steel bourdon tube. The pressure measurements are thought to be reliable within ±0.1% full scale.

The phase compositions were determined with a Model 700 Hewlett-Packard chromatograph using a thermal conductivity cell detector. The chromatographic column was 3 ft long by 1/8 in. in diameter and was packed with Porapak QS. It was maintained at a temperature of 172 °C. The response factor for converting from area to mole fraction was 1.9889 for nitrogen relative to 1.0000 for isopentane. This factor was obtained by using pure component samples in a 0.5-mL sample loop at pressures up to about 200 mm of mercury. Over this range, the response was linear with sample size. The compositions are believed known to ±0.005 mole fraction.

Materials

The nitrogen used in this work was obtained from a local supplier and was stated to have a minimum purity of 99.99 mole %. A sample of the material was analyzed on a silica gel column and no impurity peaks were detected. The isopentane was Phillips petroleum research grade having a reported purity of 99.99+ and it was used without further treatment

Table I. Experimental Equilibrium Phase Properties for the Isopentane–Nitrogen System

Pressure, psia (P)	Composition[a]		Refractive index[b]		Molar volume[c]		Equilibrium constant	
	Liquid (x)	Vapor (y)	Liquid (n_L)	Vapor (n_V)	Liquid (V_L)	Vapor (V_V)	Nitrogen (K_{N_2})	Isopentane (K_{iC_5})
				219.6 °F				
140.5	0.0037	0.163	1.2935	1.0126	2.24	42.4	44.2	0.840
177.5	0.0085	0.310	1.2928	1.0133	2.23	34.5	36.5	0.696
247.5	0.0205	0.486	1.2918	1.0149	2.22	26.0	23.7	0.525
420.0	0.0435	0.674	1.2890	1.0185	2.20	15.0	15.5	0.341
645.5	0.0753	0.757	1.2854	1.0235	2.16	9.94	10.1	0.262
918.5	0.112	0.805	1.2805	1.0296	2.13	7.08	7.22	0.220
1319.0	0.170	0.827	1.2728	1.0394	2.07	5.03	4.86	0.209
1673.5	0.221	0.835	1.2650	1.0489	2.03	3.96	3.79	0.211
2292.5	0.300	0.830	1.2520	1.0645	1.95	3.04	2.77	0.244
3008.5	0.437	0.780	1.2197	1.1012	1.89	2.20	1.78	0.392
				159.8 °F				
73.5	0.0027	0.255	1.3188	1.0059	2.07	82.4	94.5	0.747
93.5	0.0054	0.418	1.3187	1.0063	2.07	64.3	77.5	0.585
133.5	0.0106	0.583	1.3183	1.0070	2.06	45.3	55.0	0.422
175.5	0.0153	0.675	1.3178	1.0079	2.05	34.7	44.1	0.330
241.5	0.0238	0.752	1.3169	1.0092	2.05	25.5	31.6	0.254
386.5	0.0420	0.831	1.3150	1.0120	2.03	16.1	19.8	0.176
573.5	0.0598	0.879	1.3126	1.0158	2.01	10.7	14.7	0.129
804.5	0.0929	0.899	1.3098	1.0206	1.97	7.71	9.68	0.111
1127.5	0.130	0.912	1.3054	1.0272	1.93	5.59	7.02	0.101
1584.5	0.185	0.918	1.2983	1.0373	1.87	4.01	4.96	0.101
2014.5	0.238	0.919	1.2914	1.0472	1.82	3.16	3.86	0.105
2530.0	0.297	0.916	1.2825	1.0601	1.76	2.51	3.09	0.119
3013.5	0.350	0.905	1.2728	1.0736	1.72	2.13	2.59	0.146
				99.8 °F				
32.5	0.0010	0.322	1.3405	1.0019	1.94	237	322	0.679
47.5	0.0030	0.546	1.3404	1.0022	1.94	150	182	0.455
75.5	0.0062	0.725	1.3400	1.0027	1.94	89.7	117	0.277
119.5	0.0113	0.824	1.3396	1.0036	1.93	54.2	72.9	0.178
199.5	0.0226	0.892	1.3390	1.0054	1.92	30.2	39.5	0.110
349.5	0.0373	0.931	1.3373	1.0083	1.90	17.1	25.0	0.072
547.5	0.0597	0.949	1.3353	1.0123	1.88	10.8	15.9	0.0543
886.5	0.0970	0.962	1.3315	1.0192	1.84	6.58	9.92	0.0423
1399.5	0.152	0.965	1.3255	1.0300	1.78	4.17	6.35	0.0415
1914.5	0.192	0.965	1.3194	1.0410	1.74	3.05	5.02	0.0440
2286.5	0.244	0.961	1.3147	1.0493	1.67	2.58	3.95	0.0516
2633.5	0.276	0.958	1.3103	1.0572	1.64	2.25	3.47	0.0583
3013.5	0.305	0.953	1.3052	1.0661	1.61	1.99	3.12	0.0676
				40.0 °F				
26.5	0.0024	0.822	1.3612	1.0008	1.83	244	342	0.178
66.0	0.0051	0.931	1.3609	1.0020	1.83	69.6	182	0.070
143.5	0.0152	0.968	1.3601	1.0036	1.82	33.7	63.7	0.033
278.0	0.0354	0.982	1.3587	1.0063	1.79	18.0	27.7	0.019
466.0	0.0504	0.986	1.3568	1.0102	1.78	11.0	19.6	0.015
806.5	0.0866	0.991	1.3536	1.0174	1.74	6.29	11.4	0.0096
1329.0	0.143	0.994	1.3486	1.0288	1.67	3.77	6.96	0.0070
1899.5	0.201	0.991	1.3431	1.0415	1.61	2.67	4.94	0.0104
2318.5	0.240	0.985	1.3389	1.0509	1.56	2.25	4.11	0.0195
2673.5	0.260	0.987	1.3355	1.0584	1.54	1.95	3.79	0.0172
2973.5	0.281	0.982	1.3325	1.0657	1.52	1.78	3.49	0.0248

[a] Mole fraction nitrogen. [b] Relative to vacuum at 6328 Å. [c] ft^3 lb-mol^{-1} calculated from the refractive index and composition data.

Experimental Results

The behavior of mixtures of nitrogen and isopentane was studied at temperatures of 40.0, 99.8, 159.8, and 219.6 °F. The experimental phase compositions were used to calculate the vapor–liquid equilibrium ratios. The phase compositions together with the measured refractive indices of each phase were used to calculate the equilibrium phase molar volumes. All of the experimental measurements and the calculated results are presented in Table I. Example pressure–composition diagrams are shown graphically at two temperatures in Figure 1, and the calculated equilibrium ratios are shown for all temperatures in Figure 2.

The molar volumes of the phases were calculated from the composition and refractive index measurements using the Lorentz–Lorenz molar refractivity relationship as follows:

$$R_{LL}{}^0 = \frac{M}{\rho} \frac{n^2 - 1}{n^2 + 1}$$

In determining the density of the mixtures it was assumed that the refractivities were additive on a molal basis. The development and use of these relationships have been explained in the work of Keilich (9) and Smyth et al. (10) and their applicability to hydrocarbon–nonhydrocarbon systems has been justified further by Besserer and Robinson (2). The molal refractivity of
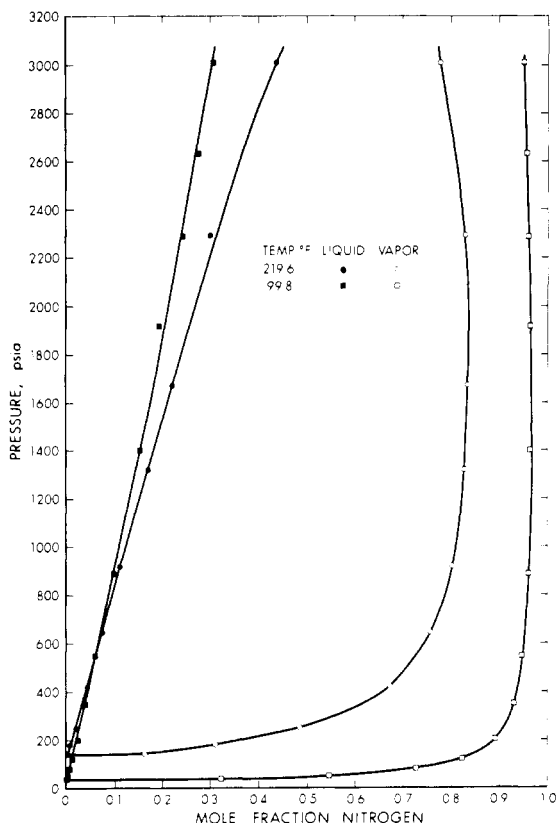
Figure 1. Pressure–equilibrium phase composition diagram for the nitrogen–isopentane binary system at two temperatures.

Figure 2. Equilibrium ratios for nitrogen and isopentane in the nitrogen–isopentane binary system.

Table II. Consistency Test of Nitrogen–Isopentane Experimental Data

Temp, °F	No. of exptl points	Points passing test
40.0	11	8
99.8	13	9
159.8	13	11
219.6	10	6

Table III. Henry's Constants at Zero Pressure for Nitrogen in Isopentane

Temp. °F	Henry's constant, psia	
	Graphical	Analytical
40.0	9700	8250
99.8	8910	7780
159.8	7720	7960
219.6	6730	6940

isopentane was obtained by measuring the refractive index of the pure material at each temperature up to a pressure of about 3000 psia. These measurements were then used with density values for isopentane calculated from the Benedict–Webb–Rubin (1) equation of state with recently established coefficients (6) to calculate the molar refractivity at each temperature. The values obtained along each isotherm were fitted as a linear function of pressure and R_{LL}^0 determined at zero pressure. At the wavelength of 6328 Å which was used in this work the values of R_{LL}^0 ranged from 25.17 mL g-mol^{-1} at 40° to 25.44 mL g-mol^{-1} at 220 °F. These are the same as those reported by Besserer and Robinson in an earlier paper (4).

A similar procedure was used to determine the refractivity of nitrogen but the influence of temperature and pressure was so small that the constant value of 4.44 mL g-mol^{-1} reported by Besserer and Robinson (5) was used throughout.

The reliability of the molal volumes calculated in this way is expected to be within about 0.5% for the liquid phase and 1.5% for the vapor phase. In the case of some of the low pressure points for the vapor phase where the refractive index is close to unity, the error may be as high as 5%.

Discussion

The entire set of P–x–y data at each temperature was subjected to the thermodynamic consistency test proposed by Christiansen and Fredenslund (7). The calculated vapor com-
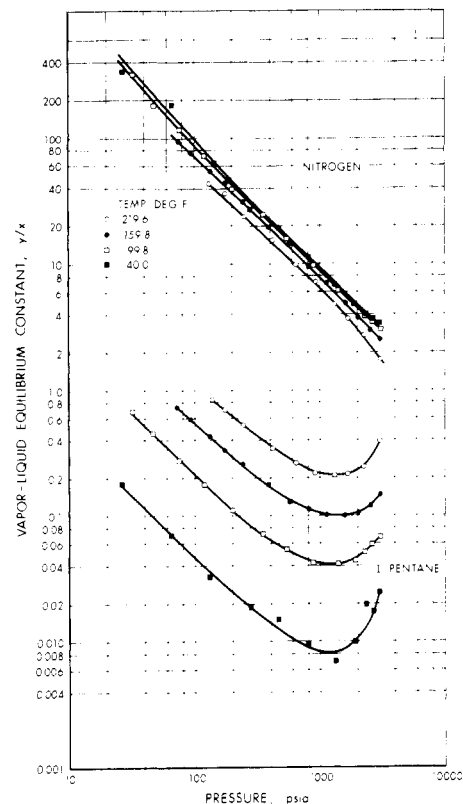
positions were compared with the experimentally measured values at each pressure and temperature. If the difference between these two values is less than the sum of the expected absolute experimental error in vapor composition plus the error in liquid composition the data point is said to be consistent. The results of these tests are given in Table II which shows that the data are generally consistent with about 75% of the points passing the test.

The points that failed to pass the test did not show any pattern with temperature or pressure and were more or less randomly distributed over the entire temperature and pressure region. The most common reason for a point failing to pass the test seemed to be that the concentration of nitrogen in the liquid phase was very low such that minor changes in liquid composition gave relatively large errors in predicted vapor composition. The test for this system is also particularly stringent because of the sharp curvature of the dew point locus at the lower pressures.

In addition to the above tests, the Henry's constant for nitrogen in isopentane at zero pressure was calculated at each temperature, Table III. The values were obtained graphically by plotting f_2^0/x_2 vs. x_2 and extrapolating to zero solute concentration and analytically using the method of Christiansen and Fredenslund (7). Considerable difference exists between the values obtained using the two methods. The values of f_2^0/x_2 used for the graphical determination showed very little scatter and estab-

lished a well-defined line which could easily be extrapolated to zero pressure. However, the values of f_2^0/x_2 obtained from the analytical calculations did not establish good lines and it is believed considerable error resulted from the interpretation given by the program to points at very low concentrations. For this reason, the values of Henry's constant obtained graphically are considered to be the more reliable.

Glossary

f_2^0	fugacity of solute at zero pressure
K_{N_2}	equilibrium ratio for nitrogen
$K_{i-C_5H_{12}}$	equilibrium ratio for isopentane
M	molecular weight
n	refractive index
n_L	refractive index of liquid
n_V	refractive index of vapor
P	pressure
R_{LL}^0	Lorentz–Lorenz molal refractivity at zero pressure
V_L	molal volume of liquid
V_V	molal volume of vapor
x	mole fraction of component in liquid phase
x_2	mole fraction of solute in liquid phase
y	mole fraction of component in vapor phase
ρ	molal density

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Vapor–Liquid Equilibrium of Petroleum Fractions Single Fraction and Binary Systems

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Narrow boiling petroleum fractions were obtained from a straight run cut (30–350 °C) and were thoroughly characterized. The vapor pressure of the narrow boiling petroleum fractions was measured in an equilibrium cell and compared with that of the corresponding pure component at different temperatures. Considering the petroleum fractions as pseudo-components, the vapor–liquid equilibria of binary systems containing petroleum fractions were studied at subatmospheric pressures. The modified regular solution model was found to represent the resulting activity coefficients.

At the present time, the most widely used correlation to predict the vapor–liquid equilibrium of petroleum fractions is that presented in 1961 by Chao and Seader (3). This is because the Chao–Seader correlation predicts the vapor–liquid equilibrium ratios of multicomponent systems from a knowledge of the pure component properties, i.e., from pure "pseudo-components" properties in the case of petroleum fractions.

The most recent trend of vapor–liquid equilibrium correlations uses pure component data together with binary data in the form of experimentally obtained binary interaction parameters (5, 11), to predict the vapor–liquid equilibrium of multicomponent systems. Unfortunately, however, these new techniques are not generally applicable to systems containing petroleum fractions. The major difficulty lies not in the ability of the correlation to accommodate petroleum fractions, but rather in establishing the necessary binary interaction parameters. The problem then lies in defining and calculating a binary interaction parameter to be used for petroleum fractions (10).

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A method has been presented that can allow the generation of binary vapor–liquid equilibrium data for systems containing pseudo-components (petroleum fractions). The experimental data were accurately represented by a modified regular-solution model for liquid-phase activity coefficients.

Experimental Section

The equilibrium still used in this investigation is of the vapor recirculating type (6, 8, 9). It is made of glass and designed so that the contactor is self-lagged with its own vapor. The temperature of the liquid in the contactor was measured with an accuracy of ±0.1 °C by a calibrated iron-to-constantan thermocouple. The pressure in the still was measured by an open U-tube mercury manometer and a precision cathetometer. The overall accuracy in the pressure measurements was better than ±0.2 mmHg. A microset electrical manostat was used to control the pressure in the still. The operation of the still was checked with pure single components and a binary system (7).

A Hewlett-Packard Model 5750 gas chromatograph (GC), equipped with two flame ionization detectors and connected to a digital integrator, was used in characterization and analysis. Two identical 10 ft long stainless steel columns, packed with 5% OV-101 (dimethyl silicone fluid) on 80/100 Chromosorb W-HP, were used in the analysis. The GC was calibrated using mixtures of known compositions of the petroleum fractions to be analyzed. From the calibrations, it was deduced that the accuracy of the analyses is ±0.3 mole % for F4–F8 and F5–F9 and ±0.5 mole % for n-C7–F5 and benzene–F5 (6).

The four petroleum fractions used in this study were obtained by distilling a wide-boiling light fraction of a Libyan crude oil called Nafoora. Some of the important properties of the crude oil and the Nafoora light fraction are given in Table I (6).

The four petroleum fractions used were characterized by measuring their specific gravity, their content of aromatics,