the Jones-Dole equation applied up to 0.1*m* for the rare earth chlorides and perchlorates but has already broken down in the nitrates because of complexation at much lower concentrations. Consequently, the data of this research could not be used to evaluate significant Jones-Dole parameters for the nitrates.

At higher molalities the rare earth nitrate viscosities increase from La to Lu at constant molality (neglecting the possible crossings near saturation mentioned above). A high concentration modification in behavior is beginning to occur in the rare earth chlorides (*13, 19*) and becomes fully established in the perchlorates (*18*) by 3.5*m*. At these high concentrations, the rare earth perchlorate viscosity at constant molality rises from La to Nd, decreases to Tb, and then rises again to Lu. Related effects also appear in the electrical conductances of these salts (*15, 16*).

This behavior was attributed to a general increase in viscosity across the rare earth series owing to a net increase in the number of waters bound by the rare earth ion as the lanthanide contraction gives rise to an increase in the surface charge density on the ion. This increase in viscosity across the series is modified by a change in the inner sphere hydration number between Nd and Tb and gives rise to both the high concentration two-series behavior and the S shape at lower concentrations. This mechanism involves the retention of the complete inner sphere hydration sheath of the rare earth ions at all concentrations. The retention of the hydration sheath by the rare earth ions has recently been confirmed by X-ray diffraction studies of nearly saturated rare earth chloride solutions (*6*) and a nearly saturated rare earth perchlorate solution (*7*). That is, anions do not penetrate the inner hydration sphere of the rare earth ions in solutions of these stoichiometric salts.

The absence of the same two-series behavior in the nitrates is not very surprising since the nitrate ions probably penetrate the rare earth ion's inner hydration sphere and displace water. The release of this inner sphere water into the system also qualitatively accounts for the fact that the viscosity of each rare earth nitrate is lower than that of the corresponding chloride and perchlorate. Since electrical conductance data give more direct information about changes in complexation across the rare earth series, the nitrate viscosities will be discussed in more detail when the conductances are being considered (*9*).

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Equilibrium-Phase Properties of Isopentane–Carbon Dioxide System

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Vapor and liquid equilibrium-phase compositions and refractive indices were determined for the isopentane–carbon dioxide system at 40.0°, 100.0°, 160.1°, and 220.1°F from the vapor pressure of isopentane to pressures in the critical region. The equilibrium ratios were calculated for each component at each temperature from the phase composition data. The equilibrium-phase densities were calculated from the measured phase composition and refractive index by use of the Lorentz-Lorenz molar refractivity relationship.

A systematic study of the literature pertaining to the phase behavior relationships of carbon dioxide–paraffin hydrocarbon binaries did not reveal any published data on the carbon dioxide–isopentane system. Data of this kind are useful for the evaluation of binary interaction coefficients required in equation of state or other generalized vapor-liquid equilibrium correlations and for the determination of the Henry's Law constant for carbon dioxide dissolved in isopentane. Accordingly, it was decided to carry out an experimental study of the system in the temperature range from 40° to 220°F.

Experimental Method

The experimental equipment and procedures were essentially the same as those described in earlier papers by Besserer and Robinson (*1, 5*). Measurements were made at each of four temperatures which were nominally 40°, 100°, 160°, and 220°F. At each temperature, measurements of the equilibrium-phase compositions and refractive indices were made at a series of pressures between the vapor pressure of isopentane and the vapor pressure

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of carbon dioxide or the critical pressure for the system. The temperature was measured with a calibrated pair of iron-constantan thermocouples with the reference junction kept in an ice bath, and it is believed known to ±0.1°F. The pressure was measured with a strain gauge pressure transducer calibrated against the vapor pressure of carbon dioxide at 70°F and is believed known to ±3 psi.

The phase compositions were determined with a Hewlett-Packard Model 700 gas chromatograph equipped with a thermal conductivity cell detector. The column was made from 3-ft by ⅛-in. diameter stainless-steel tubing packed with Poropak QS maintained at 170°C. The response factors for conversion from area fraction to mole fraction were 1.821 for isopentane compared to 1.000 for carbon dioxide. These factors were obtained by using

Table I. Experimental Equilibrium-Phase Properties for *i*-Pentane–Carbon Dioxide System

	Composition[a]		Refractive index[b]		Molar volume[c]		Equilibrium constant	
Press, P	x	y	n_L	n_V	V_L	V_v	K_{CO_2}	$K_{i\text{-}C_5H_{12}}$
40.0°F								
6.1	0.0000	0.0000	...	...	...	...	...	1.0000
22	0.0187	0.7073	1.36144	1.00135	1.795	213.7	37.824	0.2983
44	0.0461	0.8614	1.35943	1.00209	1.767	105.6	18.685	0.1453
85	0.0961	0.9279	1.35536	1.00341	1.717	56.02	9.648	0.0805
160	0.2031	0.9563	1.34581	1.00589	1.610	30.27	4.709	0.0548
239	0.3176	0.9705	1.33413	1.00890	1.496	19.32	3.056	0.0432
309	0.4458	0.9793	1.31984	1.01177	1.365	14.29	2.197	0.0374
382	0.6077	0.9809	1.29758	1.01522	1.198	11.00	1.614	0.0487
464	0.8225	0.9832	1.25708	1.01960	0.9782	8.500	1.195	0.0946
505	0.9063	0.9870	1.23532	1.02194	0.8955	7.520	1.089	0.1387
541	0.9706	0.9959	1.21736	1.02408	0.8269	6.691	1.026	0.1395
565	1.0000	1.0000	1.21037	1.02543	0.7878	6.262	1.000	...
100.0°F								
20.3	0.0000	0.0000	...	...	...	...	...	1.0000
67	0.0350[d]	0.6771	0.33918	1.00366	1.884	83.01	19.346	0.337
123	0.0897	0.8219	1.33520	1.00544	1.826	43.87	9.163	0.1956
204	0.1510	0.8830	1.32892	1.00801	1.767	26.38	5.848	0.1378
316	0.2478	0.9206	1.31914	1.01203	1.670	16.17	3.715	0.1056
457	0.3731	0.9396	1.30375	1.01784	1.550	10.44	2.518	0.0963
612	0.5265	0.9486	1.28146	1.02535	1.402	7.195	1.802	0.1086
785	0.7023	0.9560	1.24526	1.03637	1.255	4.934	1.361	0.1478
922	0.8336	0.9662	1.20502	1.04964	1.187	3.530	1.159	0.2031
978	0.8754	0.9657	1.18915	1.05721	1.179	3.072	1.103	0.2753
1034	0.9121	0.9668	1.16761	1.06804	1.222	2.581	1.060	0.3777
160.1°F								
53	0.0000	0.0000	...	...	...	...	...	1.0000
128	0.0412[e]	0.5647	1.13545	1.00795	2.011	44.65	13.706	0.4540
213	0.0923	0.7216	1.31045	1.01052	1.961	27.05	7.818	0.3067
300	0.1434	0.7920	1.30524	1.01339	1.911	18.88	5.523	0.2428
419	0.2131	0.8386	1.29718	1.01791	1.845	12.95	3.935	0.2051
541	0.2900	0.8631	1.28760	1.02287	1.773	9.670	2.976	0.1928
709	0.3933	0.8774	1.27332	1.03069	1.678	7.004	2.231	0.2021
857	0.4848	0.8876	1.25684	1.03864	1.608	5.374	1.831	0.2182
999	0.5668	0.8944	1.23949	1.04969	1.555	4.186	1.578	0.2438
1156	0.6665	0.8883	1.21029	1.06677	1.535	3.167	1.333	0.3349
1248	0.7257	0.8796	1.18359	1.08453	1.596	2.557	1.212	0.4389
1285	0.7552	0.8618	1.17516	1.10033	1.590	2.243	1.141	0.5645
220.1°F								
114	0.9000	0.0000	...	...	...	...	...	1.0000
147	0.0107[f]	0.2115	1.29257	1.01328	2.212	38.91	19.766	0.7970
222	0.0482	0.4292	1.28850	1.01594	2.179	26.23	8.905	0.5997
331	0.0977	0.5980	1.28297	1.01937	2.134	17.63	6.121	0.4455
437	0.1506	0.6656	1.27657	1.02390	2.087	13.02	4.420	0.3937
545	0.2015	0.7124	1.26981	1.02807	2.045	10.34	3.535	0.3602
683	0.2689	0.7485	1.25996	1.03492	1.993	7.849	2.784	0.3440
858	0.3481	0.7768	1.24636	1.04444	1.942	5.919	2.232	0.3424
1025	0.4362	0.7850	1.22714	1.05682	1.912	4.550	1.800	0.3813
1190	0.5204	0.7731	1.20696	1.07520	1.895	3.523	1.486	0.4731
1290	0.5929	0.7488	1.17791	1.09556	1.998	2.901	1.263	0.6170

[a] Mole fraction carbon dioxide. [b] Relative to vacuum at 6328 Å. [c] Ft³/lb mol calculated from the refractive index and composition data. [d] Smoothed value, 0.041. [e] Smoothed value, 0.044. [f] Smoothed value, 0.15.

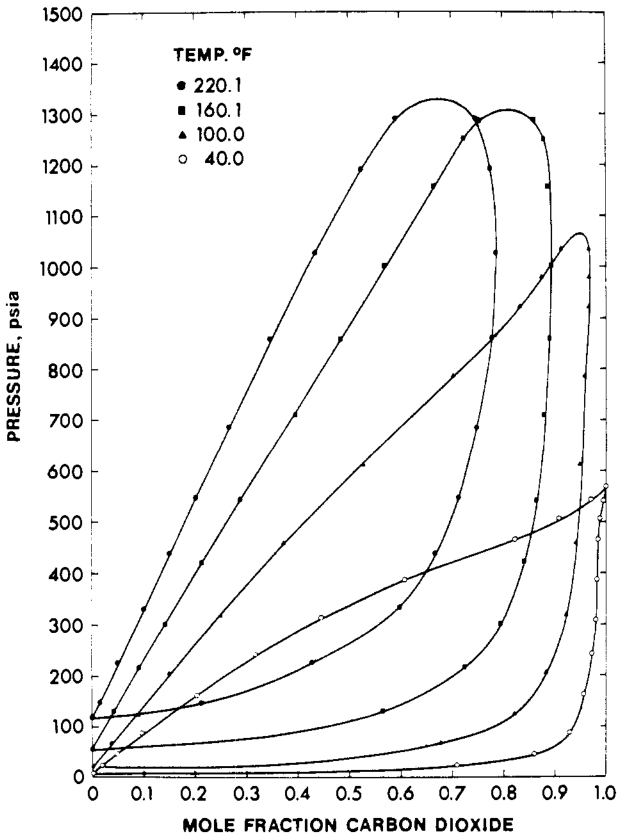

Figure 1. Pressure-equilibrium phase composition diagram for *i*-pentane-carbon dioxide system

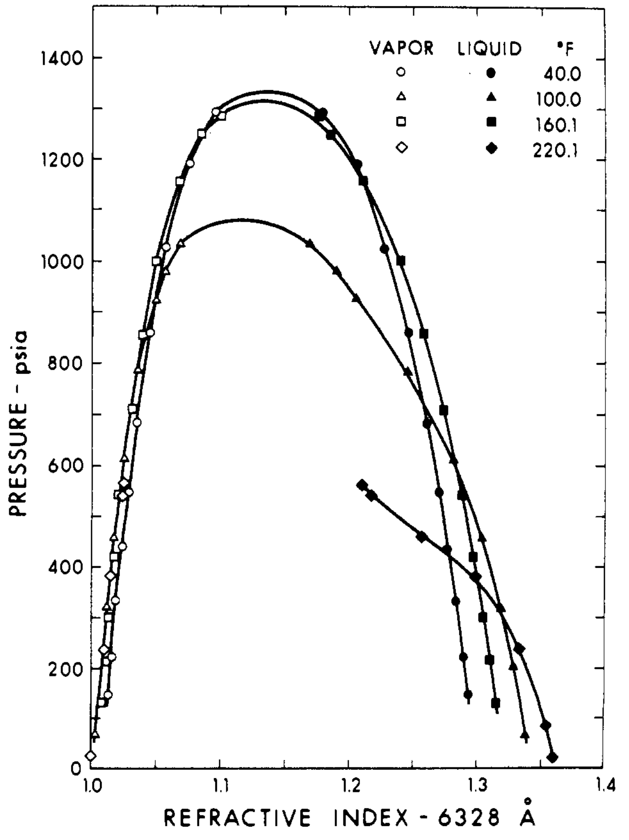

Figure 2. Pressure-equilibrium phase refractive index diagram for *i*-pentane-carbon dioxide system

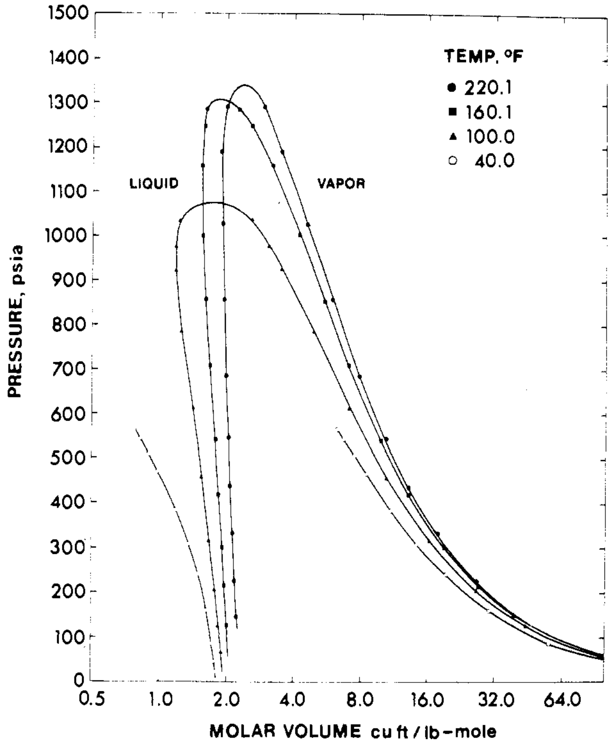

Figure 3. Pressure-equilibrium phase molar volume diagram for *i*-pentane-carbon dioxide system

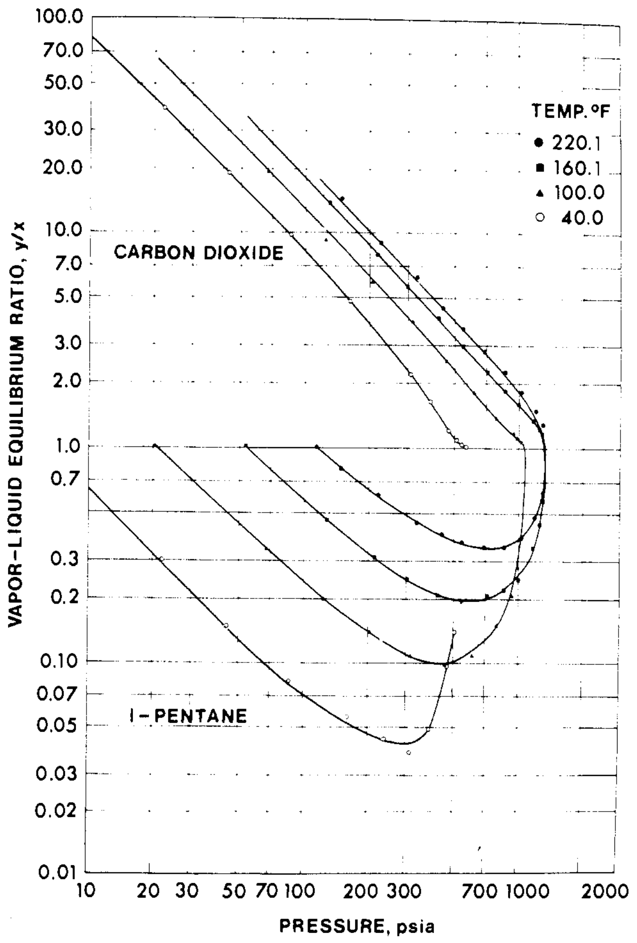

Figure 4. Equilibrium ratios for *i*-pentane and carbon dioxide in *i*-pentane-carbon dioxide binary system

Table II. Pure Component Lorentz-Lorenz Refractivities in cc/g mol at 6328 Å

Component	Temp, °F 40	100	160	220
Carbon dioxide	6.60	6.60	6.60	6.60
Isopentane	25.17	25.26	25.35	25.44

pure component samples in a 1-cc sample loop at pressures up to 0.3 atm. The compositions are believed known to ±0.003 mole fraction or better.

Experimental Results

The experimental measurements of the equilibrium-phase compositions and refractive indices, together with the calculated phase densities and vapor-liquid equilibrium ratios are given in Table I. The vapor and liquid-phase envelopes at each of the four temperatures of 40.1°, 100.2°, 159.8°, and 220.0°F are shown as a function of pressure and composition in Figure 1. Figures 2–4 show the refractive indices, calculated phase densities, and the equilibrium ratios for both isopentane and carbon dioxide.

The phase densities were calculated from the phase compositions and refractive indices by use of the Lorentz-Lorenz molar refractivity relationship described previously (*4*) and by assuming that the refractivities are additive. The molar refractivities of pure carbon dioxide and isopentane which were used are shown in Table II.

The values for carbon dioxide were obtained by using the density data for pure carbon dioxide reported by Reamer et al. (*3*) and the refractive index data reported by Besserer and Robinson (*2*). The values for isopentane were calculated by using refractive index measurements made on pure isopentane at each temperature and pressures to 1500 psia and using density information on isopentane calculated by the Benedict-Webb-Rubin equation of state. The coefficients in the equation would reproduce experimental densities in the same temperature and pressure range with an rms error of less than ±0.5%. The refractivities of carbon dioxide and isopentane were essentially independent of pressure in the interval of interest.

Discussion

The completion of this experimental study has filled in the last gap that existed in the carbon dioxide–saturated hydrocarbon binary systems for methane through *n*-pentane. This information is useful for calculating binary interaction parameters, Henry's Law constants and dilation parameters for carbon dioxide dissolved in these systems, and equation of state coefficients. Scope still remains for additional experimental work on some of the binaries to extend the temperature range, particularly in the low-temperature regions for hydrocarbons heavier than propane.

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The authors thank Hans Rempis for his assistance in taking the experimental data.

Nomenclature

K_{CO_2} = equilibrium ratio for carbon dioxide
$K_{i\text{-}C_5H_{12}}$ = equilibrium ratio for isopentane
n_L = refractive index of liquid
n_V = refractive index of vapor
x = mole fraction of component in liquid phase
y = mole fraction of component in vapor phase
V_L = molar volume of liquid, ft^3/lb mol
V_V = molar volume of vapor, ft^3/lb mol

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