Phase Behavior of Carbon Dioxide in Admixture with *n*-Butane, *n*-Decane, *n*-Butylcyclohexane, and *n*-Butylbenzene at 344 K and Approximately 9600 kPa

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Bubble point pressure data were acquired at 344 K and about 9600 kPa on ternary mixtures of carbon dioxide and *n*-butane with paraffinic (*n*-decane), naphthenic (*n*-butylcyclohexane), and aromatic (*n*-butylbenzene) compounds to determine what effect differences in compound type might have on carbon dioxide–hydrocarbon miscibility of such systems. The data on carbon dioxide–*n*-butane–*n*-decane, when compared with those from the literature, showed good agreement. This suggests that the remaining data reported here are reliable. The data were regressed by using the Soave–Redlich–Kwong equation of state to determine interaction coefficient sets for phase behavior prediction. These sets of interaction coefficients were used to calculate carbon dioxide–hydrocarbon miscibility. No significant difference in miscibility was found as the heavy hydrocarbon compound was changed from paraffinic to naphthenic to aromatic type.

Introduction

One process for enhanced oil recovery displaces the crude oil remaining in the reservoir by injecting carbon dioxide. The efficiency of such a displacement is much improved if miscibility between carbon dioxide and the crude oil is achieved. Prime variables of interest in determining miscibility are pressure, temperature, and crude oil composition. The best way to visualize the development of miscibility is to employ the pseudoternary conceptualization of Benham et al. (*1*). Refer to the ternary system depicted in Figure 1 at constant temperature and pressure where carbon dioxide is component 1 and the crude oil is divided into two parts: light and intermediate hydrocarbons as component 2 and heavy hydrocarbons as component 3. The dew curve A joins the bubble curve B at the critical point CP forming a two-phase region wherein vapor–liquid equilibrium tie lines are shown. An extension of the critical tie line to the crude oil base line at C and a tangent to the two-phase boundary from pure carbon dioxide to the crude oil base line at D form three crude oil composition ranges of interest. These are shown as line segments 3–C, C–D, and D–2 in Figure 1. The crude oil concentration range D–2 is first-contact miscible with carbon dioxide. Crude oil in the concentration range C–D can achieve miscibility by multiple equilibrium contacts with the gas phase. Crude oil in composition range 3–C cannot achieve miscibility with carbon dioxide. Point C is known as the maximum miscibility composition (MMC).

In evaluations of crude oil reservoirs as prospects for carbon dioxide miscible flooding, one experimental tool used is displacement of a crude oil sample with carbon dioxide in a slim tube packed with a porous medium. This experiment is run at various pressure levels so that the percentage recovery of crude oil can be determined as a function of displacement pressure level. The pressure at which percentage recovery of oil no longer increases is known as the minimum miscibility pressure (MMP).

For a crude oil of known composition, say, point E in Figure 1, a relationship between maximum miscibility composition and minimum miscibility pressure can be established. Although multiple-contact miscibility for this oil cannot be attained at the pressure and temperature shown, such miscibility could be attained at some higher pressure where the critical tie line extension intersects the crude oil base line at point E. This pressure would be the minimum miscibility pressure for this crude oil where the maximum miscibility composition is at point E. Clearly, the ability to predict the phase behavior of carbon dioxide–crude oil systems is important in relating minimum miscibility pressure to maximum miscibility composition.

Crude oils are mixtures of paraffinic, naphthenic, and aromatic hydrocarbons. The distribution of these three hydrocarbon types varies from crude to crude (*2*, *3*) but, on the average, 30–50 vol % of the crude is nonparaffinic. Leder and Irani (*4*) presented data showing continuous vapor–liquid critical loci for carbon dioxide–hexane, carbon dioxide–cyclohexane, and carbon dioxide–benzene binaries and intrusions of upper critical solution temperatures in the vapor–liquid critical loci for binaries comprised of carbon dioxide and naphthenic compounds of carbon number 10. Since this behavior has not been observed between carbon dioxide and paraffinic compounds of carbon numbers less than 16, Leder and Irani concluded that paraffins are more compatible with CO_2 than naphthenes. Holm and Josendal (*5*) reported data from slim tube displacement experiments, indicating that crude oil containing a more aromatic midrange fraction gave a slightly increased oil recovery when compared to data acquired on crude oil containing less aromatics. This implies a reduction in MMP as the oil is enriched in aromatics.

Work supported by the Department of Energy has been conducted over the past few years at The University of Kansas to interrelate static phase equilibrium data with slim tube flow data for the purpose of evaluating crude oil reservoirs as carbon dioxide miscible flooding prospects. Part of this work has been directed toward evaluating the effect of paraffinic, naphthenic, and aromatic hydrocarbon type on achieving carbon dioxide–oil miscibility in crude oils. Phase behavior experiments have been conducted at the Kurata Thermodynamics Laboratory on various carbon dioxide–hydrocarbon binaries where the hydrocarbons were selected from paraffinic, naphthenic, and aromatic compounds of carbon numbers ranging from 6 to 8 (*6*). The work reported herein was undertaken to determine whether the phase behavior of selected ternary systems would indicate changes in the maximum miscibility composition at constant pressure and temperature as the heavy component of the ternary system was changed from paraffinic to naphthenic to aromatic compounds of the same carbon number.

Apparatus and Procedure

Bubble point pressure data were taken at 344 K and about 9600 kPa on the ternary systems carbon dioxide–*n*-butane–*n*-decane, carbon dioxide–*n*-butane–*n*-butylcyclohexane, and carbon dioxide–*n*-butane–*n*-butylbenzene and on the five-component system carbon dioxide–*n*-butane–*n*-decane–*n*-butylcyclohexane–*n*-butylbenzene where the three hydrocarbons of

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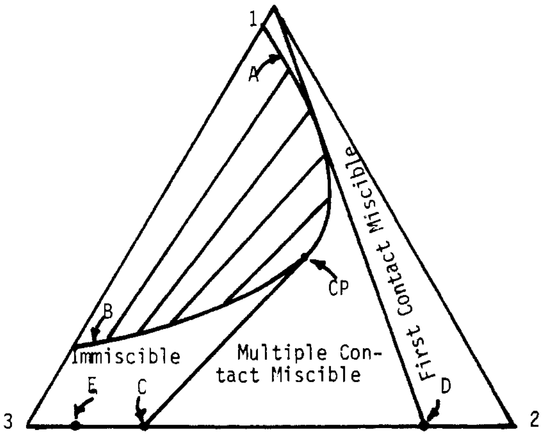

Figure 1. Pseudoternary conceptualization of Benham et al. (1).

carbon number 10 were combined in the molar ratio of 5:4:1, respectively.

The experimental design procedures of Howat and Swift (7) were used to select a priori the number and compositional locations for the data of the three ternary systems such that the interaction coefficients for the Soave-Redlich-Kwong (SRK) equation of state would be adequately defined for the purpose of this work. SRK coefficients and mixing rules were from Graboski and Daubert (8, 9) and critical constants for the chemical compounds of interest were from Reid et al. (10).

The bubble point data were taken in a blind, variable-volume cell housed in an air thermostat where temperature was controlled to ±0.02 K. Pressure of the cell content was measured with a Parascientific Digiquartz pressure transducer to ±7 kPa. The thermostat containing the cell was mounted on trunions so that it could be inverted to provide agitation of the cell contents. Ezekwe (6) and Cramer (11) describe the equipment in detail.

To make a mixture, Matheson 99.99 mol % carbon dioxide was added to the variable-volume cell at known temperature, pressure, and volume. The data of Angus et al. (12) were used to calculate the mass of carbon dioxide present. The prescribed amounts of hydrocarbons were then injected into the cell from high-pressure, variable-volume cells housed in a separate, oil-filled thermostat held at 310.9 K. These calibrated variable-volume cells served as burets to add known volumes of hydrocarbons displaced at a constant reference pressure of 8618 kPa. Phillips 99+ mol % *n*-butane was used where the data of Olds et al. (13) were used to convert volume to mass. The data of Sage et al. (14) were used to convert volume of Phillips 99+ mol % *n*-decane to mass. Aldrich 99+ mol % *n*-butylcyclohexane and Phillips 99+ mol % *n*-butylbenzene were used. Reference densities for these two materials to convert from volume to mass were measured at 8618 kPa and 310.9 K: 794 ± 3 kg/m^3 for *n*-butylcyclohexane and 854 ± 1 kg/m^3 for *n*-butylbenzene.

Bubble point pressures for the various mixtures were determined by the pressure-volume intersection method. Since the cross-sectional areas of the variable-volume cell was constant, the method reduced to measuring pressure as a function of piston position in the cell. The piston position was determined to ±0.000 025 m. Cramer (11) gives details on the procedure used to get bubble point pressures from the pressure vs. piston position data.

Results and Discussion

The measured bubble point pressures are reported in Table I. Uncertainties in temperature and pressure (reported as two standard deviations) are 0.04 K and 34 kPa, respectively. Uncertainties in composition are shown for each mixture as the last table entry.

Table I. Bubble Point Pressures at 344 K for Mixtures of Carbon Dioxide and *n*-Butane with *n*-Decane, *n*-Butylcyclohexane, and *n*-Butylbenzene

data point no.	mole fraction					p, kPa	uncert mol fr
	$x(1)$	$x(2)$	$x(3)$	$x(4)$	$x(5)$		
1	0.670	0.000	0.330			9556	0.003
2	0.674	0.068	0.258			9756	0.002
3	0.681	0.138	0.180			9618	0.002
4	0.712	0.200	0.088			9563	0.002
5	0.754	0.206	0.040			9646	0.002
6	0.753	0.207	0.040			9598	0.002
7	0.580	0.000		0.420		9646	0.010
8	0.597	0.090		0.313		9646	0.002
9	0.646	0.186		0.169		9570	0.002
10	0.702	0.219		0.079		9577	0.002
11	0.755	0.206		0.039		9742	0.002
12	0.752	0.208		0.040		9715	0.002
13	0.637	0.000		0.363		10625	0.007
14	0.614	0.000			0.386	9791	0.006
15	0.633	0.108			0.259	9694	0.002
16	0.667	0.178			0.156	9577	0.002
17	0.713	0.200			0.087	9680	0.002
18	0.782	0.192			0.025	9653	0.002
19	0.786	0.188			0.026	9666	0.002
20	0.671	0.000			0.329	10714	0.006
21	0.634	0.184			0.183	9232	0.002
22	0.754	0.205	0.0207	0.0162	0.0041	9680	0.002

A multicomponent least-squares regression program (11) was used to determine the binary interaction coefficients for the SPK equation of state which best fit the ternary system bubble point data sets of Table I.

The only ternary data found in the literature for comparison were the carbon dioxide-*n*-butane-*n*-decane data of Metcalfe and Yarborough (15). Of their data, only those at 344 K and approximately 9600 kPa could be compared directly. Table II presents the results of three regressions for carbon dioxide-*n*-butane-*n*-decane where (1) our data and those of Metcalfe and Yarborough were combined for regression, (2) our data were regressed alone, and (3) the data of Metcalfe and Yarborough were regressed alone.

The results of Table II show that the calculated pressures, root mean square errors, and interaction coefficients obtained from the three regressions are very similar. This indicates that our data and those of Metcalfe and Yarborough agree. Therefore, the other data reported in Table I should be reliable.

In the regression results which follow, only the data of Table I, excluding the last data point, were used. The results of eight regressions are reported in Table III, where regressions 4-6 are for the *n*-decane, *n*-butylcyclohexane, and *n*-butylbenzene data separately with zero hydrocarbon interaction coefficients; regressions 7-9 are for the *n*-decane, *n*-butylcyclohexane, and *n*-butylbenzene data separately with variable *n*-butane-heavy hydrocarbon interaction coefficients; regression 10 is for all data simultaneously with zero hydrocarbon interaction coefficients; and regression 11 is for all data simultaneously with variable *n*-butane-heavy hydrocarbon interaction coefficients. There was insufficient information for regression with variable interaction coefficients between the heavy hydrocarbon compounds.

Regressions 4-9 show marked variations in carbon dioxide-*n*-butane interaction coefficients as the heavy hydrocarbon component changes from paraffinic to naphthenic to aromatic. This is unacceptable within the constraints of the mixing rules being used with the SRK equation of state. Regression 10 does not represent the data within experimental uncertainity while regression 11 does represent the data within experimental uncertainty and with a root mean square error which is about the same as those for regressions 4-9. The bubble point pressure of the last data point of Table I was measured to be 9680 kPa. When we used the coefficients from regression 10, the value calculated for this composition was 9542 kPa (1.5% low) while

Table II. Regression of Carbon Dioxide-*n*-Butane-*n*-Decane Data at 344 K

mole fraction			*p*, kPa					
x(1)	*x*(2)	*x*(3)	exptl	calcd	diff, %	*k*(1,2)	*k*(1,3)	RMSE, %
				Regression 1 (*11*)				
0.670	0.000	0.330	9556	9625	+0.8	0.1244	0.1087	0.60
0.674	0.068	0.258	9756	9639	−1.2			
0.681	0.138	0.180	9618	9604	−0.2			
0.712	0.200	0.089	9563	9611	+0.6			
0.754	0.206	0.040	9646	9653	0.0			
0.753	0.207	0.040	9598	9639	+0.4			
				Regression 1 (*15*)				
0.680	0.083	0.237	9666	9715	+0.5			
0.685	0.128	0.187	9660	9687	+0.2			
0.679	0.140	0.182	9646	9563	−0.9			
0.710	0.179	0.111	9694	9749	+0.6			
0.763	0.203	0.034	9673	9653	−0.2			
				Regression 2 (*11*)				
0.670	0.000	0.330	9556	9634	+0.8	0.1246	0.1089	0.65
0.674	0.068	0.258	9756	9646	−1.1			
0.681	0.138	0.180	9618	9604	−0.1			
0.712	0.200	0.089	9563	9618	+0.4			
0.754	0.206	0.040	9646	9653	+0.1			
0.753	0.207	0.040	9598	9639	+0.5			
				Regression 3 (*15*)				
0.680	0.083	0.237	9666	9735	+0.7	0.1204	0.1099	0.55
0.685	0.128	0.187	9660	9687	+0.3			
0.679	0.140	0.182	9646	9563	−0.9			
0.710	0.179	0.111	9694	9728	+0.3			
0.763	0.203	0.034	9673	9618	−0.6			

Table III. Interaction Coefficients Obtained from Regressions 4-11 for Carbon Dioxide (1), *n*-Butane (2), *n*-Decane (3), *n*-Butylcyclohexane (4), and *n*-Butylbenzene (5)[a]

reg no.	data pt no.	*k*(1,2)	*k*(1,3)	*k*(1,4)	*k*(1,5)	*k*(2,3)	*k*(2,4)	*k*(2,5)	RMSE, %
4	1–6	0.125	0.109						0.45
5	6–13	0.087		0.092					0.61
6	14–21	0.078			0.090				0.37
7	1–6	0.070	0.108			−0.089			0.61
8	6–13	0.120		0.092			0.060		0.44
9	14–21	0.113			0.090			0.062	0.28
10	1–21	0.094	0.112	0.091	0.089				1.49
11	1–21	0.105	0.109	0.092	0.090	−0.032	0.032	0.049	0.47

[a] Data point numbers refer to those given in Table I.

the value calculated with the coefficients from regression 11 was 9653 kPa (only 0.3% low). On the basis of these observations, the interaction coefficients of regression 11 seem to best represent the experimental data although the use of nonzero *n*-butane–heavy hydrocarbon interaction coefficients is contrary to current practice in equation of state prediction of carbon dioxide–hydrocarbon phase behavior. Note that while negative interaction coefficients, e.g., the *n*-butane–*n*-decane interaction coefficient of regression 11 (Table III), are excluded in theory, they may be obtained from regression analysis since the SRK equation of state and mixing rules are, at best, semitheoretical.

Maximum miscibility compositions expressed as mole fractions of the heavy hydrocarbon components on a carbon dioxide free basis were calculated by using the various interaction coefficient sets reported in Table III in a multicomponent flash program (*11*). Particular care was taken to obtain convergence in the critical region so that tie line extrapolation by the method of Benham et al. (*1*) would be correct. These maximum miscibility compositions are reported in Table IV.

The expected uncertainty in the maximum miscibility composition calculation is 0.008 mole fraction. Therefore, there seems to be no significant difference in maximum miscibility composition as the heavy hydrocarbon compound type changes from paraffinic to naphthenic to aromatic save, perhaps, for calculations made with interaction coefficients from regressions 7–9. Those coefficients have already been disallowed because of the variation of the carbon dioxide–*n*-butane interaction coefficient as the heavy hydrocarbon compound is changed from paraffinic to naphthenic to aromatic type.

Table IV. Maximum Miscibility Composition (MMC) for Mixtures of Carbon Dioxide and *n*-Butane with *n*-Decane, *n*-Butylcyclohexane, or *n*-Butylbenzene[a]

ternary system with	MMC using			
	reg 4–6	reg 7–9	reg 10	reg 11
n-decane	0.226	0.197	0.239	0.210
n-butylcyclohexane	0.216	0.244	0.217	0.231
n-butylbenzene	0.223	0.239	0.213	0.235

[a] MMC is reported as mole fraction of heavy hydrocarbon on a carbon dioxide free basis.

Conclusions

The bubble point pressure data reported herein appear to be reliable. At 344 K and 9600 kPa there is no significant change in maximum miscibility composition as the heavy hydrocarbon compound is changed from paraffinic to naphthenic to aromatic type.

In retrospect, any change in maximum miscibility composition as the heavy component is changed from paraffinic to naphthenic to aromatic compound type will probably be increased at higher pressures (lower *n*-butane concentrations). Cramer (*11*) presented an analysis of the complete set of

Metcalfe and Yarborough (*15*) data which indicated that the interaction coefficients of the SRK equation of state mixing rules are functions of pressure. Therefore, it would be highly conjectural to make calculations of maximum miscibility composition at other pressure levels with any of the interaction coefficient sets of Table III.

Our data and those of Metcalfe and Yarborough (*15*) should be analyzed in terms of other equations of state which might better predict carbon dioxide–hydrocarbon phase behavior. More multicomponent carbon dioxide–hydrocarbon data should be acquired at other pressures and temperatures to further test equations of state being employed for phase equilibria calculations.

Glossary

k	SRK interaction coefficient, dimensionless
p	pressure, kPa
x	mole fraction, dimensionless

Suffixes

1	carbon dioxide
2	*n*-butane
3	*n*-decane
4	*n*-butylcyclohexane
5	*n*-butylbenzene

Registry No. *n*-Butane, 106-97-8; *n*-decane, 124-18-5; *n*-butylcyclohexane, 1678-93-9; *n*-butylbenzene, 104-51-8; carbon dioxide, 124-38-9.

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Adsorption of Oxygen, Nitrogen, and Argon on 5A Molecular Sieve

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A static experimental setup is described for the measurement of multicomponent adsorption equilibria. Single-component and binary isotherms on 5A molecular sieve are obtained for oxygen, nitrogen, and argon at temperatures between 0 and 75 °C and pressures ranging from 0 to 5 bar. Literature data in this range are scarce, often inaccurate, but are vital to the study of pressure swing adsorption for separation of air. Careful calibration and automation allowed us to obtain accuracies of 0.1% on pressures (electronic transducers) and 0.2% on concentrations (quadrupole mass spectrometer). The data can be fitted equally well with a multicomponent Langmuir isotherm and a model isotherm of Ruthven over this practical temperature and pressure range.

Introduction

Accurate multicomponent adsorption equilibrium data are important for use in the design and simulation of pressure swing adsorption apparatus for separation of gas or vapor mixtures (*1*). A number of these adsorption units are operated at temperatures above 0 °C and pressures of a few bar. The literature contains little information for those operating conditions. A good example is the industrially important air separation on 5A molecular sieve. Very few single-component and multicomponent data or correlations are available in this range for adsorption of oxygen, nitrogen, and argon mixtures on 5A molecular sieve (*2–6*). Only one set of data on O_2–N_2 mixtures is fairly complete but unfortunately does not agree with other literature data and our own data on the amount adsorbed (differences of about 20%). A new and accurate data set over a wide range of pressures and temperatures seems thus useful.

Since diffusion and the resulting mixing are rapid at these elevated temperatures, there is no need to use a mixing device to obtain a uniform composition in the adsorption apparatus. A static method can be used with measurement of pressures before and after introducing a known amount of gas mixture in an adsorption cell and a single measurement of the resulting gas-phase concentration. In this way, a number of technical problems encountered with recirculation methods (*7*) or chromatographic methods (*3*) are avoided. The measurement of gas-phase concentration has to be performed without disturbing the equilibrium, so only a small sample can be withdrawn, which is no problem with mass spectrometry.

Apparatus and Experimental Procedure

The experimental setup is described below with reference to Figure 1. It consists essentially of two stainless steel pressure vessels with temperature, pressure, and concentration measurements, and a number of connecting lines and valves. All lines are $^1/_8$-in. o.d. and all valves $^1/_8$-in. ball valves (Whitey, Swagelok) except valves 2, 6, 7, which are 1/16-in. miniature regulating and shut-off valves (Nupro) and their connecting lines (1/16-in. o.d., 0.25-mm i.d.), so as to minimize their holdup. Each pressure vessel is equipped with a PT100 temperature sensor (0.1 °C accuracy) and an electronic pressure transducer (Druck Ltd. U.K., PDCR 10, 0.1% accuracy).

The adsorption cell is partially filled with an accurately weighed sample of freshly regenerated adsorbent through a fill opening closed with a plug. It is placed in a thermostatic bath,

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