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Effect of Additive Gases on the Liquid–Liquid–Vapor Immiscibility of the Carbon Dioxide + *n*-Nonadecane Mixture

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Liquid–liquid–vapor phase equilibria behavior is studied for the ternary mixtures CO_2 + nitrogen + *n*-nonadecane and CO_2 + propane + *n*-nonadecane in an effort to determine the effect of additive gases on the liquid–liquid–vapor behavior seen in the binary mixture CO_2 + *n*-nonadecane. In pressure–temperature space, the ternary three-phase region develops to the low-temperature side of the binary liquid–liquid–vapor locus when nitrogen is added, whereas the addition of propane to the binary mixture results in the three-phase region developing to the high-temperature side of the binary locus. Properties reported are pressure, temperature, and compositions and molar volumes for all three fluid phases in the three-phase regions, in addition to location and characterization of the boundaries of the regions.

Introduction

The authors have undertaken an extensive study of the multiphase equilibria behavior of CO_2 + hydrocarbon mixtures. In an earlier study, the liquid–liquid–vapor (LLV) phase equilibria behavior of the binary mixture CO_2 + *n*-nonadecane was reported (*1*). In this paper, we report how this binary LLV behavior is altered by the addition of a third component, either propane or nitrogen. *n*-Nonadecane exhibits LLV immiscibility with CO_2 over a range of 12.6 K up to 32.3 °C.

There is both economic and scientific interest in how impurities, or "additive gases", affect the phase equilibria of CO_2 + crude oil systems. The ternary system of CO_2 + nitrogen + *n*-nonadecane has relevance to the problem of using nitrogen as an additive gas in a CO_2 flood in an effort to reduce the cost of the pressurizing gas. Also, during a flood the CO_2-rich gas phase in a reservoir can become enriched with light hydrocarbons such as propane after multiple contacting of the live oil. The presence of propane can expand existing three-phase behavior in pressure–temperature space or even induce it at temperatures where it would not have existed if the pressurizing gas were pure CO_2. The phase equilibria data are also useful in assessing, as well as contributing to, the flexibility of an equation of state with respect to the composition of the pressurizing gas, as might be appropriate to a reservoir simulation.

Previous work on liquefied natural gas systems (*2*) has led to an understanding of the manner in which a third component extends the three-phase region from the LLV locus of an originally immisicible binary pair. In pressure–temperature space, the three-phase region will develop to the low-temperature side of the binary locus if the third component is too molecularly dissimilar to be LLV immiscible with either one of the first two components. The ternary system of methane + *n*-hexane + *n*-octane behaves in this manner (*3*) where methane + *n*-hexane is the LLV immiscible binary mixture. This will be the case for the ternary system CO_2 + nitrogen + *n*-nonadecane.

Propane is miscible with both CO_2 and *n*-nonadecane and therefore the three-phase region will extend to the high-temperature side of the binary LLV locus. The system of methane + *n*-hexane + CO_2 is similar in nature (*3*).

Some three-phase composition data for the system of CO_2 + propane + *n*-hexadecane have been reported earlier by Meldrum and Nielsen (*4*), and recently interpreted by Orr and Jensen (*5*). Pressure–composition data are reported at 60 and 70 °F. However, no previous CO_2 + nitrogen + hydrocarbon three-phase studies exist, to the knowledge of the authors.

Experimental Apparatus and Procedures

A description of the experimental apparatus is given in an earlier paper (*6*). Some modifications were necessary to allow the study of ternary systems. These are described in ref *7*. The procedures for performing LLV studies are presented in the same reference. We briefly summarize those procedures; the apparatus employs a stoichiometric approach wherein a known amount of *n*-nonadecane is added to a visual (glass) equilibrium cell. (The volume of these cells is typically 7–8 mL.) Measured amounts of gas are added to the cell from high-pressure bombs. By careful mass balances, the composition and molar volume of the three phases can be determined from conjugate measurements at a given temperature and pressure.

Conjugate measurements involve three experimental runs in which one measurement has a large amount of L_1 relative to the L_2 and V phases. The second measurement has a large amount of L_2 relative to L_1 and V, and the third measurement has a large amount of V relative to L_1 and L_2. The analysis requires that both temperature and pressure be set, which for a ternary three-phase system defines an invariant point. Experimentally, this required the study of isotherms within the three-phase region. Data are taken at various pressures along the isotherm and then plotted. Smoothing these data makes it possible to select specific pressures at that temperature for analysis. The amount of *n*-nonadecane present in the vapor phase was found to be negligible. In subsequent calculations it was assumed that the vapor contained no hydrocarbon. The boundaries of the LLV regions were determined by straightforward visual observation.

Temperature is measured with a Pt-resistance thermometer to an estimated accuracy of ±0.02 K while pressure is mea-

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Table I. Temperature and Pressure Raw Data for the Boundary Loci of CO_2 + Nitrogen + *n*-Nonadecane

temp, K	press., bar	temp, K	press., bar	temp, K	press., bar
K points		301.36	81.39	Q Points	
294.70	91.11	301.67	81.03	293.71	90.25
296.28	88.49	301.91	80.52	293.64	88.21
297.51	86.75	302.34	80.11	293.54	86.45
298.97	84.63	302.96	78.99	293.42	82.62
299.97	83.42	303.22	78.73	293.37	79.78
300.12	83.07	303.84	77.97	293.32	77.57
300.39	82.65	304.07	77.51	293.28	74.62
300.86	82.06	304.81	76.28	293.16	72.04
301.07	81.88			293.13	69.14
				293.08	66.02
				292.99	62.45
				293.19	62.37

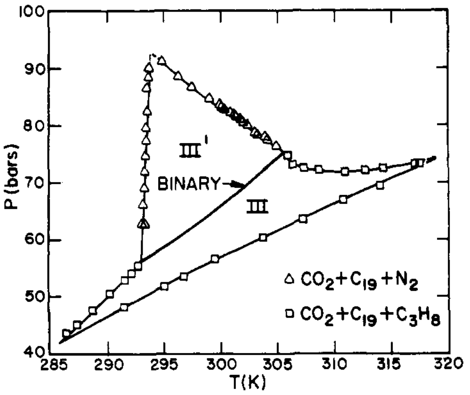

Figure 1. Pressure as a function of temperature for the liquid–liquid–vapor regions of the systems of CO_2 + nitrogen + *n*-nonadecane and CO_2 + propane + *n*-nonadecane.

sured to ±0.07 bar with pressure transducers which are frequently calibrated against a dead-weight gauge. Phase volumes in the calibrated visual cell are determined by cathetometer to an accuracy of ±0.005 mL.

Materials

The *n*-nonadecane was purchased from Alfa Products with a stated purity of 99%. Its melting point was determined to be 31.67 ± 0.05 °C. This is the same *n*-nonadecane as was used in the binary CO_2 + *n*-nonadecane LLV study of Fall et al. (*1*).

The CO_2 was obtained from Air Products and Chemicals, Inc. as "Coleman Grade" with a purity rating of 99.99%. It was transferred to an initially evacuated storage bomb as a liquid at about 0 °C. In this two-phase condition, the vapor phase was vented and discarded to removed light gas impurities. Samples of the remaining CO_2 were liquefied in the visual cell at 25.00 °C and the pressure difference in the bubble and dew points was observed. This procedure generally produced a CO_2 supply with a pressure difference ranging from 0.5 to 2.0 psi. The vapor pressure at 25.00 °C and the critical temperature and pressure agreed with the literature values (*8*) to within ±0.07 bar (1 psia) and ± 0.06 K, which is within the experimental accuracy of the visual cell technique in question for determining the location of pure component critical point.

The other gases were also obtained from Air Products and Chemicals, Inc. and were used without further purification. The nitrogen was rated at 99.998% ("Ultra High Purity") and the propane rated at 99.5% ("Instrument Grade").

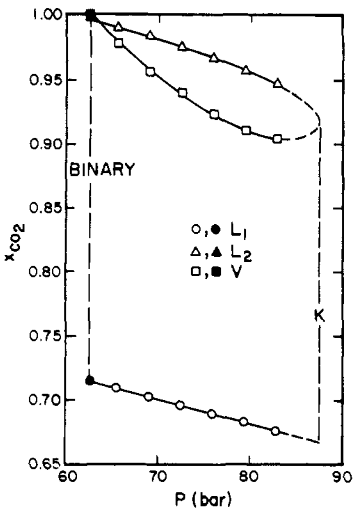

Figure 2. CO_2 mole fraction as a function of pressure for the liquid–liquid–vapor region of CO_2 + nitrogen + *n*-nonadecane at 24 °C.

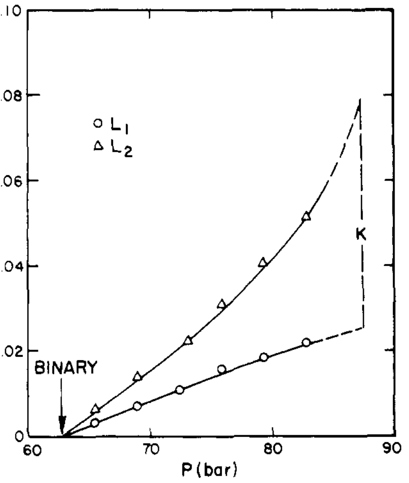

Figure 3. Nitrogen mole fraction as a function of pressure for the L_1 and L_2 phases for the liquid–liquid–vapor region of CO_2 + nitrogen + *n*-nonadecane at 24 °C.

Results

Table I presents pressure and temperature data for the K (L–L=V) and Q (SLLV) point loci which bound the three-phase region of the system CO_2 + nitrogen + *n*-nonadecane. Table II presents the temperature and pressure data for the K, LCST (L=L–V) and Q point loci which bound the three-phase region of the system CO_2 + propane + *n*-nonadecane. Figure 1 is a composite drawing in *P*–*T* space of the three-phase regions found in both ternary studies. These LCST, K, and Q point data should be considered good to ±0.05 K and ±0.1 bar. The intersections of the ternary three-phase boundaries in Figure 1 are not directly measured and should be considered estimates.

CO_2 + nitrogen + *n*-nonadecane LLV data for isotherms at 21, 24, and 28 °C are presented in Table III The compositions (mole fractions) should be considered good to ±0.002 and liquid-phase molar volumes good to ±0.8 mL/(g-mol) at 21 °C. Vapor-phase molar volumes should be good to ±4.0 mL/(g-mol) at all temperatures reported. These estimates are based on the average absolute deviation (AAD) of the raw LLV data of several experimental runs from smoothed curves of the data. Graphs of the composition and molar volume data for this system at 24 °C are presented in Figures 2–4. It should be remembered that the raw data presented is not strictly "raw", in the sense that it is derived by using some smoothing of the data within a single experimental run, as mentioned earlier.

CO_2 + propane + *n*-nonadecane LLV data for isotherms at 24, 28, 32, and 36 C are presented in Table IV. The compositions should be good to ±0.003 and molar volumes good

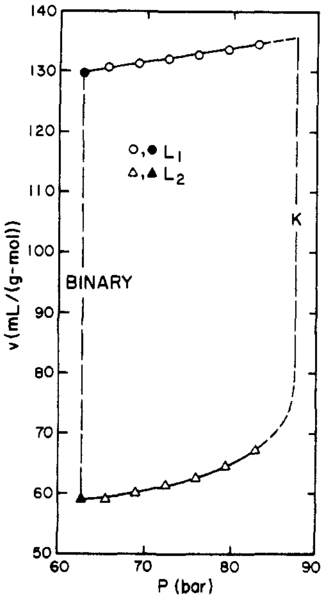

Figure 4. Molar volume as a function of pressure for the L_1 and L_2 phases for the liquid–liquid–vapor region of CO_2 + nitrogen + *n*-nonadecane at 24 °C.

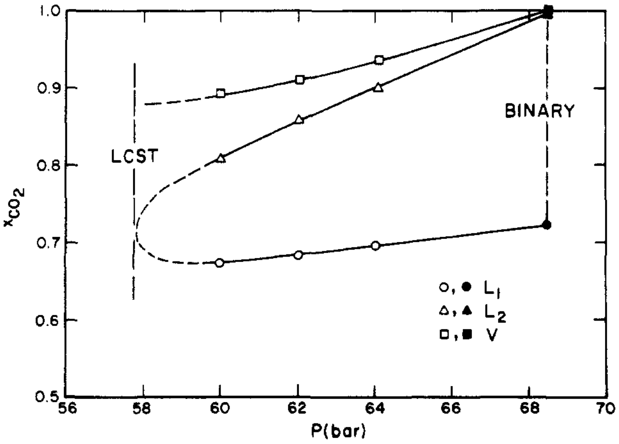

Figure 5. CO_2 mole fraction as a function of pressure for the liquid–liquid–vapor region of CO_2 + propane + *n*-nonadecane at 28 °C.

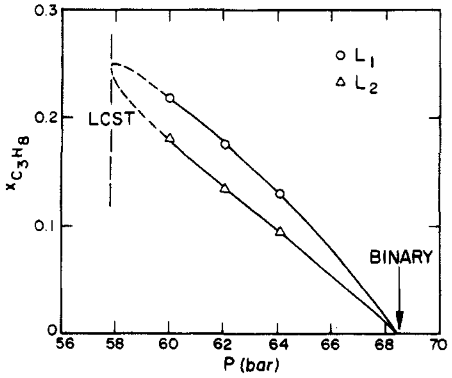

Figure 6. Propane mole fraction as a function of pressure for the L_1 and L_2 phases for the liquid–liquid–vapor region of CO_2 + propane + *n*-nonadecane at 28 °C.

to ± 1.0 mL/(g-mol). Vapor molar volumes should be good to ± 3.0 mL/(g-mol) at all temperatures reported. Graphs of the composition and molar volume data at 28 °C are presented in Figures 5–7. Figures 8–10 show the composition and molar volume data at 36 °C, where the isotherm terminates from above at a ternary K point rather than at the binary LLV locus as in the three other isotherms.

Table II. Temperature and Pressure Raw Data for the Boundary Loci of CO_2 + Propane + *n*-Nonadecane

temp, K	press., bar	temp, K	press., bar	temp, K	press., bar
K Points		Q Points		LCST Points	
305.85	74.74	286.47	43.44	291.55	48.13
306.36	73.07	287.30	44.80	295.14	51.95
307.31	72.46	288.66	47.57	296.83	53.41
308.67	72.09	290.24	50.46	299.61	56.46
310.94	71.96	291.45	53.28	303.76	60.22
312.71	72.19	291.94	54.33	307.24	63.36
314.33	72.55	292.64	55.67	310.74	66.71
317.06	73.19			314.04	69.19
317.58	73.20				

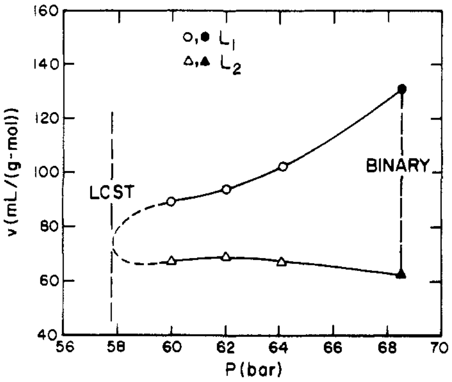

Figure 7. Molar volume as a function of pressure for the L_1 and L_2 phases for the liquid–liquid–vapor region of CO_2 + propane + *n*-nonadecane at 28 °C.

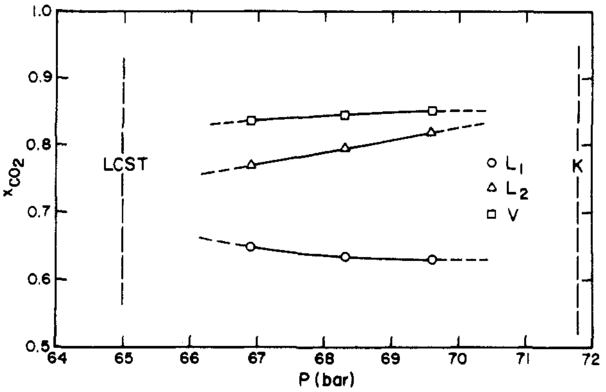

Figure 8. CO_2 mole fraction as a function of pressure for the liquid–liquid–vapor region of CO_2 + propane + *n*-nonadecane at 36 °C.

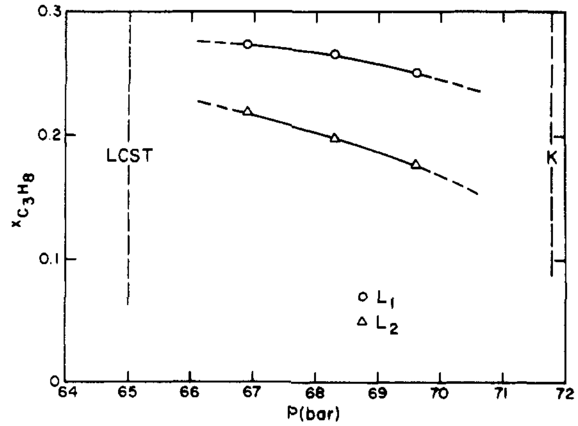

Figure 9. Propane mole fraction as a function of pressure for the L_1 and L_2 phases for the liquid–liquid–vapor region of CO_2 + propane + *n*-nonadecane at 36 °C.

As Table III indicates, extrapolative methods were used to calculate the compositions and molar volumes of the critical (L2) phase at the K points. These values, in parentheses, cannot

Table III. Pressure, Phase Compositions, and Molar Volumes for the Liquid-Liquid-Vapor Region of CO_2 + Nitrogen + n-Nonadecane

	L_1 phase			L_2 phase			V phase	
	mole fracn		mol vol,	mole fracn		mol vol,	mole fracn	mol vol,
press., bar	CO_2	N_2	mL/(g-mol)	CO_2	N_2	mL/(g-mol)	CO_2	mL/(g-mol)
Temperature = 21 °C (294.15 K)								
58.38[a]	0.7060	0.0	132.3	0.9954	0.0	57.6		
62.05	0.7041	0.0038	131.4	0.9852	0.0078	58.6	0.9699	184.7
65.50	0.6992	0.0066	132.0	0.9778	0.0153	58.9	0.9460	177.7
68.95	0.6935	0.0101	132.6	0.9705	0.0230	59.2	0.9243	170.4
72.39	0.6877	0.0133	133.4	0.9525	0.0312	59.8	0.9059	161.9
75.84	0.6833	0.0162	133.7	0.9543	0.0398	60.9	0.8900	151.9
79.29	0.6772	0.0195	134.6	0.9454	0.0490	62.2	0.8779	141.7
82.74	0.6718	0.0225	135.2	0.9358	0.0591	63.7	0.8686	131.3
86.18	0.6649	0.0256	136.4	0.9252	0.0701	66.0	0.8631	120.8
92.28[b]	0.6567[c]	0.0295[c]	138.6[c]	(0.8903)[d]	(0.1034)[d]	(77.3)[d]		
Temperature = 24 °C (297.15 K)								
62.63[a]	0.7146		129.4	0.9974		57.8		
65.50	0.7092	0.0034	130.6	0.9909	0.0063	59.0	0.9780	179.0
68.95	0.7028	0.0072	131.3	0.9833	0.0141	60.2	0.9562	168.9
72.39	0.6963	0.0108	132.1	0.9752	0.0225	61.3	0.9390	154.7
75.84	0.6896	0.0160	132.8	0.9669	0.0311	62.6	0.9232	144.6
79.29	0.6829	0.0184	133.7	0.9576	0.0406	64.6	0.9116	132.5
82.74	0.6764	0.0221	134.6	0.9471	0.0513	67.3	0.9040	120.1
87.30[b]	0.6680[c]	0.0255[c]	135.7[c]	(0.9190)[d]	(0.0808)[d]	(79.1)[d]		
Temperature = 28 °C (301.15 K)								
68.52[a]	0.7197	0.0	128.4	0.9982	0.0	62.4		
72.39	0.7137	0.0036	130.6	0.9881	0.0099	64.3	0.9782	146.9
75.84	0.7079	0.0067	131.3	0.9785	0.0195	67.2	0.9639	130.7
79.29	0.7016	0.0093	132.2	0.9684	0.0302	71.4	0.9521	114.1
81.80[b]	0.6969[c]	0.0108[c]	133.6[c]	(0.9477)[d]	(0.0488)[d]	(90.2)[d]		

[a] Binary data, interpolated from data in ref *1*. [b] K point, interpolated from K point locus data. [c] Extrapolated L_1 data. [d] Values in parentheses were calculated by using extrapolated three-phase data on L_1.

Table IV. Pressure, Phase Compositions, and Molar Volumes for the Liquid-Liquid-Vapor Region of CO_2 + Propane + n-Nonadecane

	L_1 phase			L_2 phase			V phase	
	mole fracn		mol vol,	mole fracn		mol vol,	mole fracn	mol vol,
press., bar	CO_2	C_3	mL/(g-mol)	CO_2	C_3	mL/(g-mol)	CO_2	mL/(g-mol)
Temperature = 24 °C (297.15 K)								
53.61[a]	(0.6488)[e]	(0.2761)[e]	(92.8)[e]				0.894[d]	235[d]
57.24	0.6681	0.1807	99.7	0.8603	0.1307	65.7	0.9194	213.9
58.62	0.6811	0.1443	102.5	0.8927	0.0997	63.0	0.9352	208.7
60.00	0.6918	0.1031	110.5	0.9257	0.0681	61.1	0.9570	207.9
62.63[b]	0.7146		129.4	0.9974		57.8		
Temperature = 28 °C (301.15 K)								
57.81[a]	(0.7113)[e]	(0.2484)[e]	(73.1)[e]				0.880[d]	224[d]
60.00	0.6729	0.2175	89.1	0.8085	0.1790	67.1	0.8917	203.9
62.07	0.6822	0.1754	93.6	0.8574	0.1348	69.0	0.9095	185.8
64.14	0.6920	0.1296	102.6	0.9005	0.0947	66.7	0.9350	174.8
68.52[b]	0.7197		128.4	0.9982		62.4		
Temperature = 32 °C (305.15 K)								
61.52[a]	(0.6958)[e]	(0.2546)[e]	(82.8)[e]				0.885[d]	202[d]
64.14	0.6530	0.2418	87.1	0.7782	0.2167	77.0	0.8918	177.3
66.21	0.6666	0.2003	92.5	0.8333	0.1640	75.3	0.9009	159.0
68.28	0.6802	0.1578	101.0	0.8752	0.1214	72.2	0.9152	147.6
75.17[b]	0.7225		128.0					
Temperature = 36 °C (309.15 K)								
65.00[a]	(0.7006)[e]	(0.2624)[e]	(73.5)[e]				0.824[d]	187[d]
66.90	0.6476	0.2727	85.0	0.7704	0.2183	68.8	0.8347	166.4
68.28	0.6338	0.2649	89.9	0.7959	0.1971	73.0	0.8423	151.8
69.66	0.6297	0.2501	94.3	0.8185	0.1769	75.6	0.8503	140.4
71.80[c]	0.612[d]	0.211[d]	104[d]	(0.8613)[e]	(0.1384)[e]	(101.8)[e]		

[a] LCST, interpolated from LCST locus data. [b] Binary data, interpolated from data in ref *1*. [c] K point, interpolated from K point locus data. [d] Extrapolated V data or L_1 data. [e] Values in parentheses were calculated by using extrapolated three-phase data on V or L_1.

be considered as reliable as the other entries in the table and are offered solely for the sake of completeness. This qualification also applies to the data in parentheses in Table IV for the LCST and K points. In the same sense, the dashed portions of the smoothed curves in the figures are meant to signify results not directly measured in the laboratory.

Remarks

The LLV behavior seen in these ternary systems was qualitatively as anticipated. The addition of nitrogen to CO_2 + *n*-

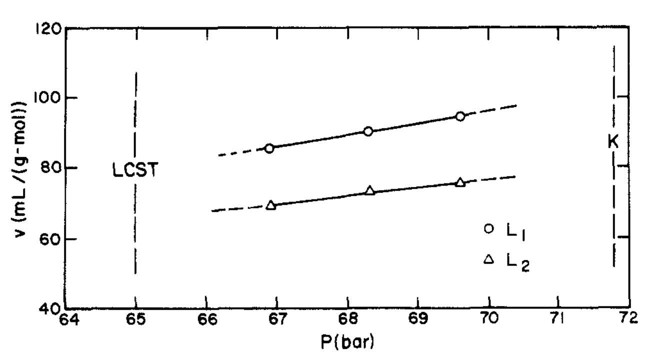

Figure 10. Molar volume as a function of pressure for the L_1 and L_2 phases for the liquid-liquid-vapor region of CO_2 + propane + *n*-nonadecane at 36 °C.

nonadecane resulted in a three-phase region developing to the low-temperature side (and high-pressure) of the binary LLV locus, while the addition of propane causes the three-phase region to extend to the high-temperature side of the LLV locus.

In terms of the CO_2 flooding of petroleum reservoirs, the data presented herein indicate that the addition of nitrogen can reduce or actually eliminate LLV behavior, while the buildup of propane in the gas phase can induce LLV behavior at temperatures where it otherwise would not have existed.

Registry No. CO_2, 124-38-9; N_2, 7727-37-9; propane, 74-98-6; *n*-nonadecane, 629-92-5.

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Excess Molar Volumes of the Mixtures Hexan-2-ol + *n*-Alkane at 298.15 K

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Values of V_m^E were determined at 298.15 K as a function of the alkanol mole fraction for the nine binary mixtures $\{xC_4H_9CH(OH)CH_3 + (1 - x)C_nH_{2n+2}\}$ from $n = 5$ to $n = 13$. V_m^E's were calculated indirectly from the density measurements effected with a vibrating-tube densimeter. Excess molar volumes were positive for the hydrocarbons with $n \geq 8$ in the entire range of compositions and sigmoidal for $5 \leq n \leq 7$.

Introduction

There are several works already done in which we have studied the behavior of hexanol isomers with different compounds (*1* – *3*). Although it is very important to know the distinct effects the presence of the hydroxyl group causes, the analysis of the interactions caused by an alkanol isomeric with another substance must begin by considering an *n*-alkane as the second component. For this reason, there are several works in the literature stating the investigations of the behavior of some mixtures of this type: *n*-alkanol + *n*-alkene (*4*), *n*-alkanol + alkane isomers (*5*), alkanol isomers + *n*-alkane (*6*), and alkanol isomers + alkane isomers (*7*). In this paper, we report the excess molar volumes at 298.15 K of hexan-2-ol + C_nH_{2n+2} (where $5 \leq n \leq 13$) fitting the experimental values by a suitable equation.

Experimental Section

All products used were from Fluka, excepting the *n*-heptane. The characteristics, indicated by Fluka, were >99.5 mol % for C_5, C_6, C_8, and C_{13}, and >98 mol % for C_9, C_{10}, C_{11}, C_{12}, and hexan-2-ol. *n*-Heptane (Riedel-de Haën, AG) was purified before use by washing with 10% Na_2CO_3 solution, drying with anhydrous magnesium sulfate, and rectifying twice in a packed column with a height equivalent to 120 theoretical plates, the final purity being 98.7 mol %. Prior to use, all products were degassed and kept in darkness on a molecular sieve (Union Carbide, Type A4, from Fluka). The properties of all pure compounds used agreed satisfactorily with the values found in the literature (*8*, *9*).

The measuring equipment and technique used were the same indicated in previous papers (*1*, *2*); however, the calibration of the densimeter was done using water and *n*-nonane