Literature Cited

(1) Franks, F., Ives, D. J. G., *Quart. Rev. (London)*, **20**, 1 (1966).
(2) Glasstone, S., "Thermodynamics for Chemists," p 433, Van Nostrand, New York, N.Y., 1947.
(3) Kientz, M. L., Bigelow, C. C., *Biochem.*, **5**, 3494 (1966).
(4) Nakanishi, K., *Bull. Chem. Soc. Jap.*, **33**, 793 (1960).
(5) Nakanishi, K., Kato, N., Murayama, M., *J. Phys. Chem.*, **71**, 814 (1967).
(6) Nêmethy, G., *Comment. Pontifica Acad. Sci.*, in press (1973).
(7) Ray, A., Nêmethy, G., *J. Phys. Chem.*, **75**, 809 (1971).
(8) Ray, A., Nêmethy, G., *Biochem.*, submitted for publication (1973).
(9) Timasheff, S. N., Inoue, H., *ibid.*, **7**, 2501 (1966).
(10) Worthing, A. G., Geffner, J., "Treatment of Experimental Data," p 260, Wiley, New York, N.Y., 1943.

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Phase-Equilibria Behavior of Systems Carbon Dioxide-*n*-Eicosane and Carbon Dioxide-*n*-Decane-*n*-Eicosane

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The phase-equilibria behavior of the binary mixture CO_2–*n*-eicosane was studied for vapor-liquid, solid-liquid-vapor, and liquid-liquid-vapor systems. The ternary mixture CO_2–*n*-decane–*n*-eicosane was studied for the liquid-liquid-vapor system in the temperature range of 29–33°C, and CO_2-free selectivities between the liquid phases are presented. Liquid CO_2 demonstrated a marked tendency toward selectivity which suggests possible separational design applications.

Phase-equilibria studies of CO_2–paraffin mixtures have been conducted by a large number of investigators, involving paraffins ranging from methane to hexadecane. Partial miscibility has been observed in mixtures of the heavier paraffins with CO_2 and suggests the use of CO_2 as an extractive agent, its success being dependent upon the selectivity of CO_2 with respect to different hydrocarbons between liquid phases.

The purpose of this paper is to present data on the binary system CO_2–*n*-eicosane and the ternary system CO_2–*n*-decane–*n*-eicosane which we feel support the proposed use of CO_2 as an extractive agent. The initial choice of a paraffinic mixture in the ternary system was based on the desire to understand better the phase behavior of CO_2–paraffin systems; our long-range plan is to study diverse hydrocarbon mixtures, e.g., aromatic–paraffinic, with CO_2 to establish broad selectivity criteria which would aid in separational process design for petroleum fractions in general.

The citation of previous phase-equilibria studies of CO_2–paraffin systems will be restricted to those exhibiting partial miscibility phenomena. Reamer and Sage (*7*) extensively studied the CO_2–*n*-decane binary system, obtaining P-V-T-x data for vapor-liquid equilibria up to 460°F. Stewart and Neilsen (*9*) reported solubility data at 60° and 90°F for binary systems of CO_2 with *n*-octane, *n*-decane, *n*-dodecane, *n*-tetradecane, and *n*-hexadecane, including partial miscibility data for the last two systems. Schneider (*8*) obtained P-T-x binary-phase equilibrium data for CO_2 in *n*-octane, *n*-undecane, *n*-tridecane, and *n*-hexadecane in the temperature range $-120°$ to 400°C at pressures up to 3700 atm. Partial miscibility phenomena were observed in all systems studied.

Ternary studies were conducted by Meldrum and Nielsen (*6*) who investigated the liquid-liquid-vapor region of the systems involving CO_2 with the paraffin pairs propane–*n*-hexadecane and *n*-decane–*n*-hexadecane. Gupta (*2*) studied the coexistence region for the ternary systems CO_2 with *n*-hexane–*n*-hexadecane, *n*-decane–*n*-hexadecane, and *n*-dodecane–*n*-hexadecane. A general treatise on the immiscibility of CO_2 in 461 ternary systems was presented by Francis (*1*), in which different types of immiscibility behavior are categorized.

Our choice of *n*-decane as one of our paraffinic components was governed by the availability of the excellent volumetric data of Reamer and Sage (*7*). Similar treatment of the system CO_2–eicosane was deemed necessary by us since volumetric data are not only useful for design purposes but also are needed to apply correlative solution models. Our binary study involves the experimental determination of the vapor-liquid, liquid-liquid-vapor, and solid-liquid vapor equilibrium of the CO_2–*n*-eicosane system. We are unaware of any systematic treatment of the system CO_2–*n*-eicosane. P-T-V-x data are taken for the phases in equilibrium, and critical points such as the type-K singular point, as well as the Q point for this system, were determined. It is hoped that a detailed study of the CO_2–*n*-eicosane system, in combination with the previously cited CO_2–*n*-decane study, would lend additional insight into the behavior of CO_2 mixtures with intermediate normal paraffins, for which only solubility data presently exist.

The primary focus of the ternary study is on liquid-liquid-vapor systems, specifically the selectivity of the liquid phases. Hydrocarbon selectivities were determined from samples on a CO_2-free basis.

Experimental Apparatus

The apparatus used in this study is the same as that used in earlier studies (*3–5*). Briefly, a P-V-T apparatus was used in conjunction with a viewable 10-cm^3 glass equilibrium cell. Temperature was measured with a Pt-resistance thermometer to ±0.05°C. Pressure was measured with Bourdon tube gauges, which were frequently calibrated against an accurate dead-weight gauge, to ±0.07 atm. The viewable glass cell was carefully calibrated and judged to be accurate to $\pm 0.02\ cm^3$. This configuration was used for all binary runs and also the ternary "scanning" runs, the latter being used to provide information on the thermodynamic location of the L1-L2-

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V region. Knowledge of this region is essential to employing a Jurgensen sight glass gauge adopted for this work (5). L1-L2-V systems were recreated in this gauge which permitted, through its design, sampling of the two liquid phases for composition determination. The CO_2 in the samples taken was allowed to outgas, and the remaining hydrocarbon mixture was analyzed with a Beckman GC-2A gas chromatograph.

Materials

The carbon dioxide used in this study was obtained from the Matheson Co. as "Coleman grade" material with a stated minimum mole purity of 99.99%. Oxygen, nitrogen, carbon monoxide, and hydrogen were the major impurities.

The carbon dioxide was prepared for use by flashing the CO_2 from the main cylinder at room temperature to the 3000-cm^3 storage reservoir maintained at 0°C. In doing this, it was hoped that the resulting liquefication of the carbon dioxide would be free of the impurities that would remain in the vapor phase. Subsequent venting of the vapor space in the reservoir would then remove these impurities.

The *n*-eicosane and *n*-decane used in this study were Humphrey-Wilkinson products labeled as having 99% minimum mole purity. The melting point of *n*-eicosane at atmospheric pressure was 36.58°C. Both *n*-decane and *n*-eicosane were used without further purification.

Binary Results: CO_2–*n*-Eicosane

Isotherms at 37°, 50°, 75°, and 100°C were taken from the liquid-vapor region, and the smoothed data are presented in Tables I–IV, respectively. It was assumed that the vapor phase was always pure CO_2.

The solid-liquid-vapor locus was found by varying conditions until a single crystal of solid was apparent. It was assumed to be pure *n*-eicosane and not to alter the liquid-phase composition. Table V presents smoothed values of pressure, temperature, liquid composition, and liquid molar volume.

In the above measurements, the estimated error in mole fractions is ±0.0014, whereas the estimated error in molar volumes is ±0.41 cm^3/g-mol. The standard deviations from the smoothed values of pressure, mole

Table I. Smoothed Values of Pressure, Composition, and Molar Volume for Liquid-Vapor Isotherm of Carbon Dioxide–*n*-Eicosane

Temperature, 37°C		
Press, atm	CO_2 liquid mole fraction	Liquid molar vol, cm^3 mol^{-1}
5.0	0.067	340.6
10.0	0.134	319.5
15.0	0.196	300.0
20.0	0.253	282.1
25.0	0.301	266.9
30.0	0.348	252.1
35.0	0.392	238.3
40.0	0.435	224.7
45.0	0.486	208.7
50.0	0.517	198.9
55.0	0.555	186.9
60.0	0.588	176.5
65.0	0.619	166.8
70.0	0.649	157.3
75.0	0.679	147.8

Table II. Smoothed Values of Pressure, Composition, and Molar Volume for Liquid-Vapor Isotherm of Carbon Dioxide–*n*-Eicosane

Temperature, 50°C		
Press, atm	CO_2 liquid mole fraction	Liquid molar vol, cm^3 mol^{-1}
5.0	0.060	346.6
10.0	0.119	327.8
15.0	0.175	309.0
20.0	0.230	292.4
25.0	0.278	277.1
30.0	0.323	262.8
35.0	0.364	249.8
40.0	0.401	238.0
45.0	0.436	226.8
50.0	0.470	216.0
55.0	0.501	206.1
60.0	0.531	196.6
65.0	0.560	187.3
70.0	0.585	179.4
75.0	0.613	170.5

Table III. Smoothed Values of Pressure, Composition, and Molar Volume for Liquid-Vapor Isotherm of Carbon Dioxide–*n*-Eicosane

Temperature, 75°C		
Press, atm	CO_2 liquid mole fraction	Liquid molar vol, cm^3 mol^{-1}
5.0	0.050	359.8
10.0	0.100	343.5
15.0	0.149	327.5
20.0	0.190	314.1
25.0	0.229	301.4
30.0	0.267	289.0
35.0	0.302	277.6
40.0	0.330	268.4
45.0	0.367	256.3
50.0	0.399	245.9
55.0	0.425	237.4
60.0	0.450	229.2
65.0	0.475	221.1
70.0	0.500	212.9
75.0	0.525	204.7

Table IV. Smoothed Values of Pressure, Composition, and Molar Volume for Liquid-Vapor Isotherm of Carbon Dioxide–*n*-Eicosane

Temperature, 100°C		
Press, atm	CO_2 liquid mole fraction	Liquid molar vol, cm^3 mol^{-1}
5.0	0.036	371.6
10.0	0.072	359.7
15.0	0.108	347.7
20.0	0.147	334.8
25.0	0.183	322.9
30.0	0.218	311.3
35.0	0.252	300.1
40.0	0.283	289.8
45.0	0.311	280.5
50.0	0.339	271.3
55.0	0.364	263.0
60.0	0.386	255.7
65.0	0.409	248.1
70.0	0.430	241.1
75.0	0.452	233.8

fraction, and liquid molar volume are ±0.46 atm, ±0.003, and ±0.57 cm^3/g-mol, respectively.

The liquid-liquid-vapor locus is presented in smoothed data form in Table VI. The procedure employed here to establish the stoichiometry of the two liquid phases was to operate the system in such a manner that, in turn, phase L1 or phase L2 is infinitesimal with respect to the other. This philosophy parallels that of the S-L-V system study. Naturally, separate charges had to be made to study L1 and L2, respectively. In addition to the error estimates above, the standard deviations for the mole fractions of L1 and L2 are ±0.0008 and ±0.0002, respectively, whereas the standard deviation for the molar volume of both phases is ±0.5 cm^3/g-mol.

The Q-point (existence of four phases: V-L1-L2-S) is labeled in Table VI. The K point, at which point the lighter liquid phase (L2) becomes indistinguishable from the vapor phase, was witnessed at a temperature just exceeding 32.15°C, at which point the boundary between the L2 phase and the vapor became cloudy and assumed a brownish hue.

Table V. Smoothed Values of Pressure, Temperature, Composition, and Molar Volume on Surface of Solid-Liquid 1-Vapor for Carbon Dioxide-*n*-Eicosane

Press, atm	Temp, °C	CO_2 mole fraction	Liquid molar volume, cm^3 mol^{-1}
5.0	36.00	0.069	337.1
10.0	35.37	0.127	320.5
15.0	34.61	0.188	301.6
20.0	33.85	0.245	284.2
25.0	33.18	0.295	269.0
30.0	32.52	0.339	255.1
35.0	31.88	0.384	241.2
40.0	31.19	0.429	227.1
45.0	30.41	0.479	212.1
50.0	29.61	0.534	195.2
55.0	28.82	0.591	178.2
60.0	28.02	0.646	161.9
65.0	27.40	0.699	145.4

Table VI. Smoothed Values of Pressure, Temperature, Compositions, and Liquid Molar Volumes on Surface of Liquid 1-Liquid 2-Vapor for Carbon Dioxide-*n*-Eicosane

Press, atm	Temp, °C	CO_2 mole fraction		Liquid molar vol, cm^3 mol^{-1}		Comment
		L1	L2	L1	L2	
66.6	27.25	0.704	0.998	139.5	63.5	Q-point
67.0	27.51	0.704	0.998	139.7	63.7	
67.5	27.85	0.704	0.998	139.8	64.0	
68.0	28.19	0.705	0.998	139.9	64.4	
68.5	28.52	0.705	0.999	139.8	64.9	
69.0	28.84	0.705	0.999	139.8	65.4	
69.5	29.17	0.705	0.999	139.7	66.0	
70.0	29.48	0.705	0.999	139.5	66.6	
70.5	29.80	0.706	0.999	139.2	67.3	
71.0	30.12	0.709	0.999	138.9	68.0	
71.5	30.43	0.710	0.999	138.4	68.9	
72.0	30.72	0.711	0.999	137.8	70.0	
72.5	31.02	0.712	0.999	137.0	71.1	
73.0	31.31	0.714	0.999	136.1	72.9	
73.5	31.60	0.717	0.999	135.0	75.0	
74.0	31.90	0.719	0.999	133.5	78.3	
74.5	32.15	0.723	0.999	131.6	82.0	

Table VII. Selectivities (β) of CO_2 for C_{10} as Function of Initial Overall Mole Ratio x_{10}/x_{20}

Initial mole ratio, x_{10}/x_{20}	Selectivity		
	29°C	31°C	33°C
0.1	4.2	4.6	5.3
0.2	4.3	4.7	5.4
0.3	4.3	4.7	5.5
0.4	4.4	4.8	5.6
0.5	4.5	4.9	5.7
0.6	4.6	5.0	5.9
0.7	4.7	5.0	6.0
0.8	4.8	5.1	6.1
0.9	4.9	5.2	6.2
1.0	4.9	5.3	6.4

Ternary Results: CO_2-*n*-Decane-*n*-Eicosane

After "scanning" runs were performed for three different initial mole ratios of x_{10}/x_{20} to determine the pressure and temperature regime where the liquid-liquid-vapor region existed, sampling runs were performed with the Jurgensen sight glass gauge for seven initial mole ratios at three different temperatures to assess the separational effect between the liquid phases. Specifically, values of the separability β on a CO_2-free basis,

$$\beta = (x_{10}/x_{20})_{L2}/(x_{10}/x_{20})_{L1}$$

where $x_{10} + x_{20} = 1$ in a phase, were the goal. The ratios (x_{10}/x_{20}) for each phase were fit with polynomials for each temperature. Since the lighter liquid phase L2 was lean in hydrocarbons, there was an expected lack of good reproducibility with respect to $(x_{10}/x_{20})_{L2}$. The average absolute difference experienced in reproducing mole ratios was ±0.017 for the L1 phase and ±0.28 for the L2 phase. Table VII gives the value of CO_2-free β as a function of initial mole ratio x_{10}/x_{20} at temperatures of 29°, 31°, and 33°C. The error in the selectivities is estimated to be ±0.35.

Remarks

CO_2 demonstrates potential usefulness as a selective liquid solvent. At this time, a discouraging feature is the leanness of the L2 phase. However, the investigators have found that outgassing of CO_2 via release of pressure is quick and clean, providing immediately fresh CO_2 for recycling in a separational process.

This study is an initial investigation into the use of CO_2 as an extracting solvent for hydrocarbon mixtures. Work has already commenced on studying aromatic-paraffinic mixtures, and considerable effort is being made to correlate the selectivity behavior with well-known solution models.

Literature Cited

(1) Francis, A. W., *J. Phys. Chem.*, **58**, 1099 (1954).
(2) Gupta, V. S., PhD thesis, Pennsylvania State University, University Park, Pa., 1969.
(3) Huie, N. C., PhD thesis, University of Notre Dame, Notre Dame, Ind., 1972.
(4) Lee, K. H., Kohn, J. P., *J. Chem. Eng. Data*, **14**, 292 (1969).
(5) McCaffrey, D. S., Kohn, J. P., *Chem. Eng. Progr., Symp. Ser.*, **64** (88), 22 (1968).
(6) Meldrum, A. H., Nielsen, R. F., *Prod. Mon.*, **19** (10), 22 (1955).
(7) Reamer, H. H., Sage, B. H., *J. Chem. Eng. Data*, **8**, 500 (1963).
(8) Schneider, G. M., *Forschr. Chem. Forsch.*, **13**, 559 (1970).
(9) Stewart, W. C., Nielsen, R. J., *Prod. Mon.*, **18** (3), 27 (1954).

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